Depiction of Chlorophyll in Nanofiber of Polymethylmethacrylate (PMMA)

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Research Article

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Abstract

The widespread application of poly methyl methacrylate (PMMA) attracted the exerting efforts here to investigate the ability of production Nano fibers of this polymer material enhanced by natural chlorophyll pigment. The work aimed to construct a general visualization about the allowed bound of the addition of the natural chlorophyll pigment to PMMA nanofiber by presenting a general statistical model. Different chlorophyll concentrations were added to the matrix material throughout preparing the specimens. Production of nanofibers has been concocted by using the electrospinning technique. The reliable assessment norm in this paper is the extent of compatibility of the additive concentration in the used polymer. The results of viscosity of the variant solutions, images of Scanning electronic microscope SEM, Analysis of Fourier Transformation Infrared Radiation FT-IR, demonstrated their subordination to the Gaussian distribution versus the chlorophyll concentration. The distinctive allocation revealed two asymmetric plateaus. The smaller first one represented the manner properties of the homogenous Nano fibers. However, the great plateau symbolized the behavior of the heterogeneous specimens. The gained regions determined the allowed limits of the homogeneity and heterogeneity of the Nano fibers depending on the additive chlorophyll concentration.

1 Introduction

The electrospinning technique has a characteristic tactic based on the electrostatic force to produce Nanofiber. The molten polymer or its solution is the raw material for that special production of fibers. The latter has a so great surface area and extremely thin fibers in comparison to the spinning fibers, which are produced by conventional methods. The procedure occurs at room temperature under normal atmospheric conditions. The application of high voltage on the tip of the needle from where polymer comes out toward the drum causes deformation of the terminal polymeric droplet. The alteration is a direct outcome of electric field interactions. Nevertheless, there are number of subordinate causes that ensue. The first parameters are those of a solution such as viscosity, solution elasticity, solution surface tension, conductivity of polymer, solvent, solution, solution temperature, added salts in solution, and vapour pressure of the solution. The second parameters are in the process, like the shape of the collector, geometry spinnerets, solution flow rate, tip-to-collector distance, and applied voltage. Thirdly, the ambient parameters are environment temperature, environment humidity, and air velocity [1–3]. According to the research of Fong et al [4], a concentration of polymer plays an effective role in the figuration of beads in the general structure of the produced nanofiber. Their experiments refer to a converse relationship between these correlated variables. They prove that the POE polymer of concentrations ranged from 1-4.5 weight percent versus viscosity of 1mPa up to 1.25 Pa. It is found that the least value of viscosity 13 mPa produced at a concentration of 1 weight percent. The obtained fibers have the highest deformation of beads and vice versa. The higher viscosity of 1.25 Pa at a concentration of 4 weight percent gives
Nano fibers with lower potential beads. Increasing viscosity diverges the distance between those beads in addition to decreasing their diameter. Perhaps it is helpful to indicate that the viscosity affects the shape of beads as well. The progressive growth of viscosity converts spherical beads gradually to spindle-like ones. Nano fiber gets uniform and larger diameter with increasing viscosity or the solution concentration. Nano fibers, produced by an electro spinning technique, are within a continual specific range of concentrations that can be determined by the viscosity of the polymeric solution. The lowering viscosity of the solution indicates the domination of the surface tension factor, which leads to beads, or the formation of beaded fibers. Exceeding of solution concentration of the critical limit fabricates a structure of nonstop fibers. The morphology of this texture is correlated to the solution concentration[3].

Within the multiplicity of the determinants of the success of electro spinning, viscosity is included as a condition that must be met at least at its minimum level of the polymer solution by providing a reasonable solubility of the polymer. In this field, solvents play an important role; on the other hand, the technique of electro spinning imposes choosing the solvent[5].

The conjugated polymers are recognized by their limitation of solubility, decline in average molecular weight, and high rigidity for their backbone. These characterized properties hinder the necessarily probable entanglements to form the electro spinning fibers. Conjugated polymer produces breaking, and discontinuous jets through resisting the strength elongation [6].

The natural pigment of chlorophyll falls within the conjugated polymers due to the existence of a porphyria structure that permits the excitation of electrons throughout the absorption process of electromagnetic waves. This framework has conjugated bonds that are the main reason for absorbing the sunlight wavelength of red, blue, and purple. That is why chlorophyll acquires its importance in plants. Moreover, it can be used as a proposed optical material that is in the present under investigation to be added as an absorber used in solar cells and light-emitting diode (LED) applications[7].

This paper presented investigates the effects of the addition of chlorophyll pigment into the PMMA at different weight concentrations. The name of Nano fiber specimens and their solutions has been taken into account according to the weight ratio of the chlorophyll to the PMMA (pure PMMA, 0.31 w%, 0.63
w%, 0.94 w%, 1.25 w%, and 1.56 w%), regardless the weight of evaporated solvent of acetone in the Nanofibers.

The relationship of viscosity changed versus the shear flow of each of the different solution concentrations as well as the viscosity change according to the chlorophyll concentrations. In addition, SEM and FT-IR analyses of the same specimens have been considered as well.

2 Method and materials

Six specimens of different weight concentrations were prepared of poly (methyl methacrylate) (PMMA) as a matrix material and chlorophyll, an additive pigment. They have been produced by electro spinning technique. The used solvent was acetone (CH$_3$)$_2$CO, and the weight ratio of the chlorophyll in the solutions is (0, 0.05, 0.1, 0.15, 0.2, 0.25 w%). The reference specimen concentration is 16 w%, a pure PMMA dissolved in the acetone.

2.1 Extraction of the chlorophyll

The extraction procedure includes immersing cleaned and dried slices of basil leaves in a caped glass tube containing acetone. The glass tube itself was immersed in a beaker full of boiled water to be left for two hours. The temperature of the water has been raised whenever water is getting cooled down. The solution has been left in the tube for forty-eight hours in a dark place at room temperature. Ultimately, the juice of chlorophyll has been isolated from the original leaves' rest by using a cotton cloth. The extracted juice of chlorophyll has been kept in a fridge.

2.2 Determining the chlorophyll concentration

Simply, this has been achieved by drying 1 mL of the juice. By calculating the difference in juice weight before and after the drying process, the concentration of the chlorophyll was 1 g/L.

2.3 Preparation of specimens' solution

Poly (methyl methacrylate), MW 25000 type ALPHA Chemistry (Germany) has been dissolved by solvent acetone at room temperature by using a magnetic stirrer. The process lasted three hours. After accomplishing the complete dissolving of PMMA, chlorophyll has been added in a progressive way. The pigment addition was adjusted according to the stated weight rates in Section 2.

2.4 Electro spinning

The electrospinning has been performed for the PMMA of weight concentration of 16 w%. In addition, the other solutions of different values of the additive concentrations. The traveled distance of the jet between the tip of the syringe and the drum was 80 mm. The electrospinning was attained under the effect of 30 kV and different values of flow rates,

Table 1: Electro spun of variant chlorophyll concentration versus different flow rate.
2.5 Characterization of the samples

The transaction involved analyzing and evaluating the results of measuring the viscosity of prepared solutions for the injection of the electro spinning by the instrument (cone plate, Brokfeld Co., Germany). Imaging of SEM, and performing FT-IR analysis for the produced nanofiber (spectrometer, Bruker, Germany).

3 Results and discussion

3.1 The viscosity of the prepared solutions

After the addition of the chlorophyll in the PMMA solution of six different specimens in their chlorophyll weight rate percent, it was important to identify their rheological property of viscosity. The results showed two different groups. The first group involves specimens of pure PMMA, 0.31, 0.63, and 0.94 w%. That has decreasing viscosity versus increasing the shear flow, so-called shear thinning or pseudoplastic, Fig. 1.

This rheological property occurs in order colloids and stabilized suspensions. It depends on the physical interaction of the chains of polymer with the added particles belonging to another phase. This case creates a model of two layers, the surface of additive particles carries a kind of charge, and the inverse kind of charge would be attained at the surrounding polymer particles. In this way, the solution acquires stabilization by producing a long-range force. This description could be attributed to the appearance style of the previously stated figure of the first group. However, approaching particles and layers to each other, by raising the concentration of the additives, converses the attractive force to the repulsive force. This interaction is well described by Hamaker's theory [8]. This refers to the establishment of the repelled force that causes the sedimentation of additives within an unstabilized suspension. Consequently, this suspension appears the kind of viscosity, seeming shear thickening or dilatant [9].

This last demeanor is recognized as a second group of specimens 1.25 w%, and 1.56 w% which shows increasing viscosity with the increasing shear flow. This phenomenon is named shear thickening or dilatant, Fig. 2.

The frequent accumulation of chlorophyll in PMMA leads to an aggregation of solute particles by a transition state from immobile to mobile particles. The predictable convergence among the forming hydro cluster increases up to the incompressible limit due to the rise of shear flow[10]. In this work, the shear thickening at its initial stage due to the low relative concentration of chlorophyll, Fig. 3. Fitting shows the

<table>
<thead>
<tr>
<th>Specimen Type w%</th>
<th>0</th>
<th>0.05</th>
<th>0.1</th>
<th>0.15</th>
<th>0.2</th>
<th>0.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate (mL/h)</td>
<td>25</td>
<td>42</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>30</td>
</tr>
</tbody>
</table>
highest obtainable viscosity which might be occurred by additive chlorophyll up to ca. 0.4 w%, before starting a new phase of the solution.

3.2 SEM assessment of the electrospun

After achieving the electrospinning of the stated solutions of different chlorophyll concentration, the gained fibers of electro-spun has been scanned by the Scanning Electron Microscopy, Fig. 4. The obvious fact from the last figure is the division of clarity of fibers. The reference specimen of pure PMMA and the next two specimens of chlorophyll concentration 0.31 w% and 0.63 w% are approximate without beads or spots of sedimentation.

There are some differences can be documented among the last three specimens. Even though, their impurity is common. However, it is clear that the irregularity of the nanofibers 0.94 w% appeared as perfusion wetting the nanofibers. This anomaly developed at nanofibers 1.25 w% to be as masses which then transforms somewhat in the nanofibers 1.56 w% to masses less number or more divergent among them, and perhaps with smaller size [8].

3.3 FT-IR analysis for nanofibers

FT-IR analysis is necessary for this characterization to prove the existence of chlorophyll in the electrospun nanofibers. In spite of the low used concentrations of chlorophyll, traces of its presence can be noticed. If there were any physical bonding between the PMMA solution and the chlorophyll, then the peaks of PMMA would be displaced. However, peaks of chlorophyll are invisible for the domination of the PMMA molecules, Fig. 5. The last figure showed some of the important molecules of PMMA [11].

The similarity of peaks over all the charts of different chlorophyll concentrations means occurring of a physical interaction. Tracking shifting of the wavenumber values of some prominent peaks showed the change in the physical intermolecular bonding between the PMMA and the chlorophyll (hypsochromic effect), Fig. 6.

The uniform behavior of the curves in Fig. 6 indicated the areas that were depending on the viscosity of the solution. The first range is limited between the concentrations of zero chlorophyll and about 0.8 w%. The last bounds specified the quantities of added chlorophyll to yield nanofiber with extremely low quantities of impurities or beads. The shift of each of the PMMA molecules of C-O, -CH3, and C = O towered higher values of wavelength number. This alteration indicated to rise in the intermolecular bonding with the chlorophyll molecules [11]. The longer the conjugate chain, the weaker the bond. Thus, the greater values of the wavenumber of the PMMA molecular groups were obtainable. The best chlorophyll concentration is ca. 0.31 w% which has the highest solution viscosity. In this case, the best molecular overlapping happens to the colloid or immobile suspension. After the last characteristic value of the maxima of the first region, increasing chlorophyll concentration in the solution results in divergent chlorophyll molecules being aggregated. The PMMA molecules are isolated by the effect of the gravitational and Hamaker force [8]. This conduct gradually leads to decreasing the viscosity of the
solution and the transition to a new phase of the second plateau. The segregated droplets of chlorophyll created growth chains to regain the state of the more powerful bonding. The highest bonding at about 1.4 w%. Beyond this value of concentration, the additives tend to be more diverging and beads of smaller radius. In other words, have shorter molecular chains of chlorophyll and weaker intermolecular bonding with the PMMA molecules.

4. Conclusion

The procedure of data fitting for the obtained values of the viscosity, and FTIR analysis, supported by SEM images, gave a general vision of the physical intermolecular bonding of the chlorophyll and PMMA. Especially, the bonding of chlorophyll with the molecules of PMMA of C-O, CH3, and C = O. The common statistical style of the secured values subjected to the Gaussian distribution of the second order according to the chlorophyll concentration. The highest viscosity is obtained by adding the chlorophyll concentration greater than zero and less than ca. 0.4 w%. However, the expectable value approaches the 0.8 w% giving nanofiber with extremely low beads. In other words, boosting the viscosity gave better nanofiber of chlorophyll additive.

Declarations

Author Declarations section

Ethical approval:

All authors declare that all the ethical standards required for the preparation and publication have been complied with. The manuscript has not been published elsewhere nor is it under consideration in any other journal.

Consent to participate:

The authors have given their consent for participation.

Consent for publication:

All authors of this paper consent for publishing manuscript, tables and figures in this journal.

Competing interests:

The authors declare that they have no competing of interest.

Authors’ contributions:

Zainab Jassim extracted the chlorophyll, prepared the solutions, and prepared the figures. Mohammed Akraa executed the electrospinning process, viscosity, SEM, FTIR, and wrote the texts of manuscript.
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Availability of data and materials:

The authors declare that the data and related material not been published elsewhere nor is it under consideration in any other journal.

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References


Figures

Figure 1

Shear thinning conduct of solutions of the specimens (pure PMMA, 0.31, 0.63, and 0.94 w%).

Figure 2

Shear thickening behavior of solutions of specimens (1.25 w%, and 1.56 w%).
Figure 3

Gaussian distribution of high fitting quality depicts the statistical alteration of the viscosity according to the increment of the chlorophyll weight concentration.

Figure 4

SEM images of the produced nanofibers of different concentrations of chlorophyll.
Figure 5

FT-IR analysis of the six specimens.
The nature of Gaussian distribution nature of the shifting of molecular groups (hypsochromic effect), C-O, -CH3, and C=O versus change the chlorophyll concentration.

Figure 6