

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE**  
**ENGINEERING AND TECHNOLOGY**

**UTILIZATION OF ELECTROSPUN NANOFIBERS CONTAINING GELATIN  
OR GELATIN-CELLULOSE ACETATE FOR PREVENTING SYNERESIS IN  
TOMATO KETCHUP**

**M.Sc. THESIS**

**Saman HENDESSI**

**Department of Food Engineering**

**Food Engineering Programme**

**JANUARY 2014**



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**Saman HENDESSI**  
**(506101522)**

**Department of Food Engineering**

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**Thesis Advisor: Asst. Prof. Dr. Filiz ALTAY**

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**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**JELATİN VEYA JELATİN-SELÜLOZ ASETAT İÇEREN NANOLİFLERİN  
DOMATES KETÇAPLARINDA SİNERESİSİ ÖNLEYİCİ OLARAK  
KULLANILMASI**

**YÜKSEK LİSANS TEZİ**

**Saman HENDESSİ  
(506101522)**

**Gıda Mühendisliği Anabilim Dalı**

**Gıda Mühendisliği Programı**

**Tez Danışmanı: Yrd. Doç. Dr. Filiz ALTAY**

**OCAK 2014**



**Saman HENDESSI**, a M.Sc. student of ITU Graduate School of Food Engineering student ID **506101522** successfully defended the **thesis** entitled “**UTILIZATION OF ELECTROSPUN NANOFIBERS CONTAINING GELATIN OR GELATIN-CELLULOSE ACETATE FOR PREVENTING SYNERESIS IN TOMATO KETCHUP**”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

**Thesis Advisor :**      **Asst. Prof. Filiz ALTAY**      .....

Istanbul Technical University

**Jury Members :**      **Asst. Prof. Hatice Funda Karbancıođlu Güler**.....

Istanbul Technical University

**Asst. Prof. Serkan Ünal**      .....

Sabancı University

**Date of Submission : 16.12.2013**

**Date of Defense : 24.01.2014**





*To my beloved husband and my family,*



## **FOREWORD**

Today, nanotechnology products that are on the market are mostly gradually improved products where some form of nanotechnology enabled material or nanotechnology process is used in the manufacturing process, but still its application in foods appears to be relatively small. The main reason is the lack of enough information, and applications of nano-sized biomaterials. This study aimed to contribute to the field of food applications of nanotechnology. This study is also a part of TUBITAK(111O556) project for the COST Action MP1206.

I would never have been able to finish my master's thesis without the guidance of my advisor, help from friends, and support from my family and husband.

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Saman HENDESSI  
(Food Engineer)



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## **ABBREVIATIONS**

<b>CA</b>	: Cellulose Acetate
<b>SEM</b>	: Scanning Electron Microscopy
<b>FSEM</b>	: FieldScanning Electron Microscopy
<b>LBG</b>	: Locust Bean Gum
<b>CMC</b>	: Carboxy Methyl Cellulose
<b>AFM</b>	: Atomic Force Microscopy
<b>TEM</b>	: Transmission Electron Microscopy
<b>FTIR</b>	: Fourier Transform Infra Red
<b>NMR</b>	: Nuclear Magnetic Resonance
<b>CD</b>	: Circular Dichroism
<b>DSC</b>	: Differential Scanning Calorimetry





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# **UTILIZATION OF ELECTROSPUN GELATIN OR GELATIN CONTAINING CELLULOSE ACETATE NANOFIBER IN TOMATO KETCHUP TO PREVENT SYNERESIS**

## **SUMMARY**

Nanotechnology is science, engineering, and technology conducted at the nanoscale. Nanotechnology applications located in the center of various engineering branches, it also brings many scientists together doesn't interact so far. In addition to applications in general areas, nanoscience is also inspiring science in the fields of food and food related products. It roots from the concepts that this technology provides a sound framework for developing an understanding of the interactions and assembly behavior of food components into microstructure, which influence food structure, rheology and functional properties at the macroscopic scale. Comparing to other areas, applications of nanotechnology in foods has been limited. The main reasons for the late incorporation of food into the nanotechnology sector are issues associated with the possible labeling of the food products and consumer-health aspects. The ability to design at atomic level nanotechnology creating a new world and deeply affects standardized operating procedures. Their applications to the agriculture and food sector are relatively recent compared with their use in other areas. Nevertheless, in the last two years, the world has entered into the search for ways to take advantage of this technology in the food industry.

Nanostructures used in nanotechnology applications divided into three groups including nanoparticles, nanotubes and nanofibers. Nanofibers are defined as fibers with diameters on the order of 100 nanometers. Nanofibers especially organic nanofibers constitute a particularly interesting and versatile class of one dimensional nanomaterial. There are some different techniques to produce nanofiber. Electrospinning, a spinning technique, is a unique approach using electrostatic forces to produce fine fibers from polymer solutions or melts and the fibers thus produced have a thinner diameter (from nanometer to micrometer) and a larger surface area than those obtained from conventional spinning processes. Some properties related to solution (e.g., concentration, viscosity, electrical conductivity, surface tension, and dielectric properties), governing variables (e.g. electrical field strength, fluid flow rate, and distance to the collector plate) and ambient parameters such as humidity and temperature, can affect electrospinning process.

Tomato ketchup is a heterogeneous, spiced product, produced basically from either cold or hot extracted tomatoes; or directly from concentrates, purees or tomato paste. Many foods of commercial importance, such as tomato paste and tomato ketchup, are concentrated dispersions of insoluble matter in aqueous media. Tomato ketchup obtains its viscosity from naturally occurring pectic substances in fruits. Their rheological behavior is important during handling, storage, processing and transport of concentrated suspensions in industry.

Ketchup consists of two parts: a thick syrup and tomato fiber. The proportion of these two components and the characteristics of the syrup are the principal factors that determine the consistency of ketchup. The thickness or body of ketchup is largely determined by the viscosity of the liquid and the proportion of insoluble tomato fiber present.

Viscosity has economic implications for tomato ketchup processors because it largely determines processing yields and product quality. For this reason, different thickeners are used to increase the viscosity of the syrup, yielding more consistent products and minimizing the phenomenon of syneresis.

Serum separation or syneresis is one of the most important problems in conventionally processed tomato products and it affects both product quality and hence consumer acceptability negatively. Hydrocolloids increased the viscosity and reduced the serum loss of tomato ketchups. Hydrocolloids are a heterogeneous group of long chain polymers (polysaccharides and proteins) characterized by their property of forming viscous dispersions and/or gels when dispersed in water. Presence of a large number of hydroxyl (-OH) groups markedly increases their affinity for binding water molecules rendering them hydrophilic compounds. Further, they produce a dispersion, which is intermediate between a true solution and a suspension, and exhibits the properties of a colloid. Considering these properties, they are aptly termed as 'hydrophilic colloids' or 'hydrocolloids'.

Gelatin is a natural biopolymer made from collagens and has biological features as the collagens. It is an aqueous polymer. Gelatin does have a significant value that it is a low price biopolymer. By some post treatment method or combine with another polymer, gelatin can be used alone or as a blend component to prepare nanofiber.

Cellulose acetate is important ester of cellulose, which can be obtained by reaction of cellulose with acetic anhydride and acetic acid in the presence of sulfuric acid. Acetic acid is usually an excellent solvent for cellulose acetates with degree of acetyl substitution (DS) greater than 0.8. According to its processing, cellulose acetate can be utilized for various applications.

In this study it was investigated using gelatin and gelatin-cellulose acetate nanofibers obtained by electrospinning technique to prevent syneresis in tomato ketchup. First process factors affecting the morphology and diameter of gelatin and gelatin-cellulose acetate nanofibers was investigated.

The electrical conductivity of gelatin solutions increased with gelatin concentration. In contrast electrical conductivity results, surface tensions decreased with gelatin concentration. In this study, the gelatin solution at low concentration of 7% did not produce nanofibers, due to insufficient entanglements and high surface tension. Instead, the mixtures of drops and some fibrous structures were seen, and this is due to the viscosity of the solution being too low to generate continuous fibers.

SEM images revealed that nanofibers could be obtained from the gelatin solution at 20%. In addition, nanofiber formations under all electrospinning process conditions can be obtained at that concentration, meaning the amount of gelatin in the solution at 20% was enough to form nanofibers. It should also be noted that nanofibers became less branching, without bead and more homogenous as applied voltage increased.

The zeta potential values of dispersions with electrospun nanofibers from the gelatin solution at 20% , were higher than values for dispersions with electrospun nanofibers from the gelatin solution at 7%. However the zeta potential of dispersions with electrospun nanofibers from the gelatin-cellulose acetate solution was the highest one, 20.78 mV. For keeping a suspension in a stable or in a dispersed state the zeta potential values should be above +25 mV or below -25mV. Accordingly the closer value to the +25 mV belonged to the sample obtained from gelatin-cellulose acetate, meaning these nanofibers may suspend in a dispersed state longer comparing to the other nanofiber samples.

The diffusion coefficient value of dispersion containing electrospun nanofibers from the gelatin solution at 20% was higher than the sample containing nanofibers from the gelatin solution at 7%. However the diffusion coefficient of dispersions with electrospun nanofibers from the gelatin-cellulose acetate solution was the highest one. Accordingly, higher diffusion coefficient means higher mobility of the polymer in the suspension. It was determined that the sample obtained from gelatin-cellulose acetate, had the highest diffusion coefficient ( $1.81 \mu\text{m}^2/\text{s}$ ), and probably the highest mobility comparing to the other electrospun samples.

After preparing the ketchup samples, different two concentrations of gelatin nanofiber (0.25% and 0.5%) and gelatin- cellulose acetate nanofiber (0.5%) added to ketchup samples and stored at different two temperatures (4°C and 25°C) for one month. After each week the syneresis and rheological measurements were done. The results showed that the ketchup samples including gelatin-cellulose acetate nanofiber provided the least amount of syneresis. Moreover, syneresis values of all samples that kept at 4°C were less than samples with the same concentration nanofiber that stored at 25°C.

According to the rheological characterizations  $n$  values of ketchup samples without any nanofiber was the highest, however the  $n$  value of all samples was  $n < 1$ , which means all samples are pseudoplastic. In addition, according to the rheological measurements it was obvious that the addition of electrospun nanofibers led to a dramatic increase in the consistency index of the tomato ketchups. It is well known that the higher the total solids the better will be the quality of the end product. The highest amount of consistency index was for ketchup samples with gelatin cellulose acetate electrospun nanofiber.

In this study syneresis and consistency are factors that affected by adding electrospun nanofiber to ketchup samples. Little amount of electrospun nanofiber increase the consistency and, as a result, decrease the syneresis of tomato ketchup samples. According to the comparisons it was concluded that ketchup samples including gelatin-cellulose acetate nanofiber are more stable at 4°C. This study provided valuable information about the potential application of nanofibers as thickener in tomato ketchup.





## **JELATİN VE YA JELATİN- SELÜLOZ ASETAT İÇEREN NANOLİFLERİN DOMATES KETÇABINDA SİNERESİSİ ÖNLEMEN İÇİN KULLANILMASI**

### **ÖZET**

Nanoteknoloji, nano düzeyde yürütülen bilim, mühendislik ve teknolojiler olarak tanımlanabilir. Nanoteknoloji uygulamaları şu ana kadar çok etkileşimde olmayan birçok mühendisliği biraraya getirmiştir. Diğer alanlardaki çok çeşitli uygulamaları yanında, nanobilim gıda ve gıda ile ilişkili ürünlerde de kullanılmaya başlamıştır. Bu uygulamaların kaynağından gıdaların makroskopik ölçekteki özelliklerinin mikroskopik yapısından kaynaklanması ve bunun reoloji gibi diğer özellikleri etkilemesi gelmektedir. Diğer alanlara kıyasla nanoteknolojinin gıdalarda uygulamaları sınırlı kalmıştır. Bunun başlıca nedenleri arasında gıdaların etiketlenmesi ve tüketici sağlığı konusunda bazı endişelerin bulunması sayılabilir. Nanoteknoloji ile atomik düzeyde tasarım yapılabiliyor olması çığır açarak standart operasyon koşullarını etkilemektedir. Gıda ve tarım alanındaki uygulamaları diğer uygulamalara nispeten yenidir. Yine de, özellikle son iki yıl içinde, bu yeni teknolojinin gıdalarda nasıl kullanılıp avantaj sağlanabileceği ile ilgili çalışmalar yapılmaktadır.

Nanoteknoloji uygulamalarında kullanılan nanoyapılar üçe ayrılmaktadır: nanopartiküller, nanotüpler ve nanolifler. Nanolifler çapı 100 nm civarındaki lifler olarak tanımlanmaktadır. Nanolifler, özellikle organik nanolifler, tek boyutlu nanomateryallerin ilginç bir bileşenidir. Nanolif elde etmek için çeşitli teknikler kullanılmaktadır. Elektrodöndürme yöntemi ile, elektrostatik kuvvetlerle polimer çözeltisinden veya eriyiğinden ince çaplı (mikrometreden nanometreye kadar) ve yüzey alanı geniş lifler elde edilmektedir. Elektrodöndürme işlemi etkileyen faktörler arasında besleme çözeltisinin özellikleri (konsantrasyon, viskozite, elektriksel iletkenlik, yüzey gerilimi ve dielektrik özellikler), işlem parametreleri (elektriksel alan kuvveti, besleme hızı ve toplayıcı plaka mesafesi) ve nem ve sıcaklık gibi çevresel faktörler bulunmaktadır.

Domates ketçabı, konsantre, püre veya domates salçasından veya domatesten soğuk veya sıcak ekstraksiyon işlemi ile üretilen baharatlı ve heterojen bir gıda ürünüdür. Domates salçası ve domates ketçabı sulu ortamda çözünmeyen maddelerin büyük konsantrasyonda bulunduğu dispersiyonlardır. Ketçap viskozitesini, yapısında doğal olarak bulunan pektik maddeler oluşturur. Bu ürünün reolojik özellikleri hazırlık, depolama, işleme ve taşıma sırasında önemlidir.

Ketçap yapısal olarak ikiye ayrılabilir: kıvamlı şurup ve domates lifi. Bu iki kısmın oranı ve şurubun karakteristikleri, ketçabın kıvamını etkilemektedir. Ketçabın yapısı veya kıvamı, sıvı kısmın viskozitesine ve mevcut bulunan çözünmeyen domates lifinin miktarına bağlıdır.

Viskozite, ketçabın işlenmesi sırasında ekonomik olarak da önemli bir parametredir. Çünkü ürün verimini ve kalitesini etkiler. Bu nedenle ketçaba, şurup kısmının viskozitesini arttıracak, daha kıvamlı bir ürün oluşturacak ve sineresisi azaltacak kıvam vericiler ilave edilmektedir.

Serum ayrılması veya sineresis, geleneksel olarak işlenen domates ürünlerinde rastlanan önemli bir problemdir. Hem ürün kalitesini hem de tüketici beğenisini olumsuz etkilemektedir. Bunun için kullanılan hidrokolloidler, hem viskoziteyi artırır hem de serum ayrılmasını azaltır. Hidrokolloidler, suda disperse olduklarında kıvamlı dispersiyonlar veya jel oluşturan yapılarıyla karakterize edilen uzun zincirli polimerlerden (polisakkaritler ve proteinler) meydana gelmiş heterojen yapıya sahip maddelerdir. Çok sayıda hidroksil gruplarının bulunması, bu maddelerin su moleküllerine bağlanmasını arttırarak hidrofilik olmalarını sağlamaktadır. Bunların oluşturdukları dispersiyonlar, gerçek çözelti ve süspansiyon arasında, kolloid özelliği göstermektedir. Bu nedenlerden dolayı bu maddeler “hidrofilik kolloidler” veya “hidrokolloidler” olarak adlandırılmaktadır.

Jelatin, kolajenden elde edilen ve özellikleri kolajene benzeyen doğal bir biyopolimerdir. Jelatin ucuz olması bakımından da özel bir öneme sahiptir. Çeşitli işlemlerden geçirilerek veya diğer polimerlerle karıştırılarak jelatinden nanolif elde edilebilmektedir.

Selüloz asetat, sülfirik asit varlığında selülozun asetik anhidrit ve asetik asitle reaksiyonu sonucunda elde edilen selülozun asetatıdır. Asetik asit, selüloz asetat için mükemmel bir çözüldür. Selüloz asetat birçok uygulamada kullanılmaktadır.

Bu tez çalışmasında elektrodöndürme yöntemiyle elde edilen jelatin ve jelatin-selüloz asetat nanolifleri ketçapta sineresis önlemek için kullanılmıştır.

Besleme çözeltisi olarak kullanılan jelatin çözeltilerinin konsantrasyonu arttıkça elektriksel iletkenlikleri de artmıştır. Buna karşın, yüzey gerilim değerleri azalmıştır. %7’lik jelatin çözeltisinden nanolif elde edilememiştir. Bunu nedeni ortamda yetersiz madde olması ve buna bağlı olarak yüzey geriliminin fazla ve viskozitesinin düşük olmasıdır.

SEM fotoğraflarından %20’lik jelatin çözeltisinden nanolif elde edilebildiği görülmüştür. Buna ilaveten bu konsantrasyonda bütün etkili parametreler değiştirilse bile nanolif elde edilebildiği belirlenmiştir. Elde edilen nanolifler, uygulanan voltaj arttıkça daha düzgün yapıda, boncuksuz ve homojen olmuşlardır.

Jelatin ve jelatin-selüloz asetat içeren nanoliflerin bulunduğu dispersiyonların zeta potansiyelleri ölçülmüştür. Sonuçlara göre, jelatin-selüloz asetat nanolifleri dispersiyonda daha stabildirler.

Nanolif içeren dispersiyonların difüzyon katsayıları karşılaştırıldığında jelatin-selüloz asetatlı örneğin difüzyon kabiliyetinin daha fazla olduğu belirlenmiştir.

Laboratuvarda hazırlanan ketçalara % 0,25 ve % 0,5 oranında jelatin nanolifi, %0,5 oranında jelatin-selüloz asetat nanolifi ilave edilmiştir. Bu örnekler iki farklı sıcaklıkta (4 ve 25 °C’de) bir ay depolanmıştır. Örneklerde her hafta sineresis ve reoloji ölçümü yapılmıştır. Sonuçlara göre, en az sineresis görülen örnek jelatin-selüloz asetat nanolif içeren örnektir. Sineresisin, düşük sıcaklıkta yüksek sıcaklığa göre daha az belirlenmiştir.

Reolojik ölçüm sonuçlarına göre, nanolif içermeyen ketçap örneklerinin n değerlerinin büyük olduğu belirlenmiştir. Ancak bütün örneklerin n değerleri 1'den küçük olduğu için hepsi psödoplastiktir. Nanolif ilavesi ketçap örneklerinin kıvam indekslerinde artışa neden olmuştur. En yüksek artış, jelatin-selüloz asetat içeren örneklerde görülmüştür.

Bu çalışmada, ketçap örneklerinin sineresisi ve kıvamlarının, nanolif ilavesiyle değiştiği tespit edilmiştir. Az miktarda bir nanolif ilavesinin ketçap örneklerinin kıvamını arttırıp sineresis azalttığı belirlenmiştir. En iyi sonuç jelatin-selüloz asetat içeren ve düşük sıcaklıkta depolanan örneklerde tespit edilmiştir. Nanoliflerin ketçaplarda sineresisi önleyici ve kıvam arttırıcı olarak kullanılabilceği sonucu gıda endüstrisi bakımından önemli bir bulgudur.



## **1. INTRODUCTION**

In 1959, the promise of nanotechnology was outlined by Nobel Prize laureate Richard Feynman in his famous talk, "There's Plenty of Room at the Bottom". Since then, the concepts of molecular nanotechnology have extended to such as "molecular engineering" by Eric K. Drexler (Drexler, 1981) and "molecular electronics" by Mark A. Ratner, (Aviram and Ratner, 1974) etc. Recently, the area of molecular nanotechnology has rapidly developed because enormous possibilities have opened to manipulate the molecular synthesis and movement. A lot of devices and applications have been demonstrated. (Heath and Ratner, 2003) It is now not an impractical dream to fabricate molecular devices and molecular machines with atomic precision.

The potential of nanotechnology to revolutionize the health care, textile, materials, information and communication technology, and energy sectors has been well publicized. In fact several products enabled by nanotechnology are already in the market, such as antibacterial dressings, transparent sunscreen lotions, stain resistant fabrics, scratch free paints for cars, and self-cleaning windows. The application of nanotechnology to the agricultural and food industries was first addressed by a United States Department of Agriculture road map published in September 2003. The prediction is that nanotechnology will transform the entire food industry, changing the way food is produced, processed, packaged, transported, and consumed. (Joseph and Morrison, 2006). There are various food or food-related products that are involved with nanotechnology in the market around the world. However, food applications appear to be limited comparing to other fields. This is probably due to the lack of regulations about nanotechnology applications in foods and insufficient studies in this area.

## **1.1. Purpose of Thesis**

The aim of this study was to evaluate the potential of nanofibers containing gelatin or gelatin-cellulose acetate (CA) as a thickener and water stabilizer in ketchups. First of all, feed solutions properties such as electrical conductivity and surface tension were determined for evaluating their effects on fiber morphology. Morphology of electrospun nanofibers was evaluated by using a scanning electron microscope (SEM). After obtaining nanofibers, the zeta potential and diffusion coefficient values of dispersion containing electrospun nanofibers from solutions were measured. And then, rheological properties and syneresis of the ketchups with nanofibers were examined.

## **2. NANOTECHNOLOGY**

Nanotechnology is the manipulation or self-assembly of individual atoms, molecules, or molecular clusters into structures to create materials and devices with new or vastly different properties. Nanotechnology can work from the top down (which means reducing the size of the smallest structures to the nanoscale e.g. photonics applications in nanoelectronics and nanoengineering) or the bottom up (which involves manipulating individual atoms and molecules into nanostructures and more closely resembles chemistry or biology). The definition of nanotechnology is based on the prefix “nano” which is from the Greek word meaning “dwarf”. In more technical terms, the word “nano” means  $10^{-9}$ , or one billionth of something. For comparison, a virus is roughly 100 nanometres (nm) in size. The word nanotechnology is generally used when referring to materials with the size of 0.1 to 100 nanometres, however it is also inherent that these materials should display different properties from bulk (or micrometric and larger) materials as a result of their size. These differences include physical strength, chemical reactivity, electrical conductance, magnetism, and optical effects (Joseph and Morrison, 2006).

### **2.1. History of Nanotechnology**

The platform for nanotechnology is believed by many workers in the field of nanotechnology to have been laid by Richard Feynman, a physicist at California Institute of Technology, in an after-dinner speech in 1959 titled, “There is plenty of room at the bottom”. Feynman is known to have explored the possibility of manipulating materials at the scale of individual atoms and molecules, imagining the whole of the Encyclopaedia Britannica written on the head of a pin and foreseeing the increasing ability to examine and control matter at the nanoscale (Sahoo et al, 2007). Smith (Smith, 2006) discussing the historical background of Feynman’s speech, the state of the art in 1959 and Feynman motivation, considered the attribution of nanotechnology to Feynman as misleading and asserted that Feynman only wished to construct microbiological machines and tools which would assist scientists in mimicking microbiological materials. Feynman in his speech offered

two prizes, one for miniaturizing the printed page of a book and another for fabrication of a micromotor of predefined size. About two and half months after the speech, McLellan, in his spare time, built the motor and presented it to Feynman (Smith, 2006). Cortie (2004) stated that miniaturization was a point that Feynman emphasized in his speech, which implied that it was not his idea. He stated that since 1800, after the pioneering studies of John Dalton, there had been intense study of the behaviour of individual atoms and molecules and their macroscopic aggregation. Despite the hype around nanotechnology in recent years, it is not a new technology. The colour effect of butterfly wings was copied by the Romans about 1600 years ago. The glass cup known as Lycurgus cup in the British Museum, due to nanoparticles of gold and silver, looks jade green in natural light and an impressive red colour when a bright light shines through it (Smith, 2006). In the manufacture of car tyres, carbon nanoparticles are included while the red and yellow colours seen at sunsets are due to nanoparticles in the atmosphere (Smith, 2006).

The term nanotechnology was first used in 1974 by Norio Taniguchi, a researcher at the University of Tokyo who used it to refer to the ability to engineer materials at nanoscale (Miyazaki, 2007; Sahoo et al, 2007).

In the 1980s, two inventions which enabled the imaging of individual atoms or molecules as well as their manipulation led to significant progress in the field of nanotechnology. (Miyazaki, 2007; Cortie, 2004; Matija, 2004) Gerd Binnig invented scanning tunnelling microscopy (STM) while Heinrich Rohrer invented atomic force microscopy (AFM). In 1985, Fullerene C<sub>60</sub> was discovered by Kroto's and Smalley's research teams. Afterwards, in 1986, Eric Drexler began to promote and popularize nanotechnology through speeches and books – “Engines of creation: the coming era of nanotechnology” (Miyazaki, 2007). In 1991, Saumio Iijima discovered carbon nanotubes and by National Nanotechnology Initiative (NNI – a Federal visionary research and development programme for nanotechnology-based investments through the coordination of 16 various US departments and independent agencies) and these paved way for the progress in research and development in the field of nanotechnology (Miyazaki, 2007; Matija, 2004; Roco, 2004).



## **2.2. Nanotechnology Application**

### **2.2.1. General application of nanotechnology**

The potential of nanotechnology to revolutionise the health care, textile, materials, information and communication technology, and energy sectors has been well-publicised. In fact several products enabled by nanotechnology are already in the market, such as antibacterial dressings, transparent sunscreen lotions, stain-resistant fabrics, scratch free paints for cars, and self cleaning windows. The application of nanotechnology to the agricultural and food industries was first addressed by a United States Department of Agriculture roadmap published in September 2003. (Url-1) The prediction is that nanotechnology will transform the entire food industry, changing the way food is produced, processed, packaged, transported, and consumed. In 2008, nanotechnology demanded over \$15 billion in worldwide research and development money (public and private) and employed over 400,000 researchers across the globe. Nanotechnologies are projected to impact at least \$3 trillion across the global economy by 2020, and nanotechnology industries worldwide may require at least 6 million workers to support them by the end of the decade (Roco et al, 2004).

The rapid development of nanotechnology since the 1990s is a topic of interest among scientists and the public. Kostoff et al. (2007) reported that nanotechnology and its applications are already incorporated into many products that are on the market. The authors also pointed out that pharmaceutical and energy industries, medicine, military, and many others actively find the use of recent advances in nanotechnology as more effective on the market compared to the traditional products. Nanotechnology has been described as the new industrial revolution, and it has been increasingly applied in food production, food processing, and food packaging (Url-2; Joseph & Morrison, 2006; Kuzma & VerHage, 2006; Sanguansri & Augustin, 2006). According to the Project on Emerging Nanotechnologies (PEN), a project of the Woodrow Wilson International Center for Scholars and the Pew Charitable Trusts, over 1,300 nanotechnology products of all types have entered the commercial marketplace all over the world, representing an increase of approximately 600% since 2006 (Url-3).

### **2.2.2. Application on nanotechnology in foods**

Food nanotechnology products are one of the biggest nanotechnology product categories. The inventory of food nanotechnology products has also increased by approximately 500% from 2006 to 2011 (Url-3). The nanotechnology food market is expected to surge from 2.6 billion USD in 2004 to 20.4 billion USD in 2010 (Url-2). An estimate by the Business Communications Company shows that the total market for nanobiotechnology products was \$19.3 billion in 2010 and is expected to reach \$29.7 billion by 2015. However, the potential market for nanotechnology food products has not been estimated (Url-4).

A number of companies around the world have realized the market potential of nanotechnology in the food industry (Sanguansri & Augustin, 2006), more than 200 companies around the world were conducting research in food nanotechnologies in 2004. This number is expected to increase to several thousand by 2010. The U.S. is the leader in nanotechnology research followed by Europe and East Asia (Url-2,3 and 4).

Nanotechnology brings dramatic changes to food production, processing and packaging (Url-2). The word “nanofood” was recently developed. The concept of a nanofood is that “nanotechnology techniques or tools are used during the cultivation, production, processing, or packaging of the food; but not modified or produced food by nanotechnology machines” (Joseph & Morrison, 2006). The application of nanotechnology also includes smart packaging, on demand preservatives, and interactive foods.

For example, bioanalytical nanotech sensors incorporated into food packaging can serve as detectors of contamination and also monitor food products through the distribution system (ElAmin, 2005; Tarver, 2006). Another application is packaging with self-cleaning surfaces, in which nanoscale coatings of dirt-repellent can protect the food from the invasion by microorganisms and ensure food safety. Nanolaminate is a type of “smart” packaging that is an extremely thin food-grade film. Nanolaminate can keep foods away from outside moisture, lipids, and gases; or it can serve as a carrier of colors, flavors, antioxidants, nutrients, and anti-microbial and improve the texture of foods (Tarver, 2006; Weiss et al., 2006).

Nanoscale particles and materials can also be used to develop custom-made foods and fresher, tastier, healthier, and safer products. Kraft Foods is experimenting with "interactive" foods that allow consumers to modify foods depend on their individual nutritional needs and tastes. For example, nanotechnology could be used to release accurately controlled amounts of the appropriate molecules to customize the smell and taste of the product for a particular consumer; it could also isolate the molecules that could cause certain allergic reaction (John, 2004; Wolfe, 2005).

Nanodispersions and nanocapsules that are made with nanoscale materials are ideal mechanisms for delivery of functional ingredients. These nanodispersions and nanocapsules can encapsulate functional ingredients such as vitamins, anti-microbials, anti-oxidants, flavorings and preservatives and release them in the body at particular sites and at precise times. Two giant food companies Nestle and Unilever are conducting research in this field to seize one part of the nanofood market (Joseph & Morrison, 2006; Tarver, 2006; Wolfe, 2005).

Nanotechnology may revolutionize technology and industry to benefit society (Url-5). In 2012, The National Nanotechnology Initiative will spend \$2.1 billion to improve the understanding of nanoscale phenomena and the capability to create nanoscale devices and systems (Url-6; Roco, 2011).

Some nanopackaging and nanofoods are already available in the commercial food market. Miller Brewing Company created a barrier technology using nanocomposite in the plastic beer bottles. Nanoparticles were embedded in plastic to provide a molecule barrier that helps prevent carbon dioxide from escaping from the beverage and prevent oxygen from seeping in. This barrier extends the shelf life of beer up to six months (Url-7). However, the success of these products and future products is affected by consumer knowledge and understanding of nanotechnology. In addition, the media plays a critical role in shaping consumer perceptions of these foods (Chaudhry et al., 2008; Dudo et al., 2010).

### **2.3. Classification of Nanomaterials**

Nanomaterials have extremely small size which having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes (Siegel, 1994).

Numerous nanosystems are now investigated, and include micelles, nanoemulsions, nanotubes, nanofibers, liposomes, dendrimers, polymer, therapeutics, nanoparticles, nanocapsules, nanospheres and hydrogels. The novel properties of nanomaterials offer many new opportunities for the food industry (Cho et al., 2008). Different types of functional nanostructures can be used as building blocks to create novel structures and introduce new functionalities into foods. These include: nanoliposomes, nanoemulsions, nanoparticles and nanofibers. Weiss has described several of these structures, their actual and potential uses in the food industry (Weiss et al., 2006; McClements et al., 2007).

#### **2.3.1. Nanofiber**

In recent years, nanotechnology has become one of the most rapidly growing fields. This technology deals with the development of materials with dimensions ranging from 1 to 100 nm. Among the various materials that have been developed, nanofibers have attracted great attention as potential building blocks for different constructs and nanodevices (Reneker and Yarin, 2008). Nanofibers are easy to fabricate and can be made with different material compositions, structures, and properties. In addition, because the surface area to volume ratio for nanofibers is inversely proportional to the fiber diameter, this ratio can be significantly increased as the fiber size is decreased. Thus, nanofibers are attractive due to their potential in many applications related to fluid absorption (Fang et al, 2008). Nanofibers can be applied as reinforcement in composites, as filtration materials, as affinity membranes, as tissue scaffolds, etc. Nanofibrous materials have shown success as fabrics for wound healing, as catalyst and enzyme carriers, as sensors, and as supports for energy storage devices (Fang et al, 2008).

However, with conventional fiber spinning technologies, fibers cannot yet be produced that have diameters less than  $2\mu\text{m}$  (Zhou and Gong, 2008). Zhou and Gong (2008) reviewed many processes to make nanofibers, such as bicomponent spinning, melt-blowing, flash spinning, and electrospinning. Among these methods, electrospinning appears to be the most efficient, the simplest, and the least expensive method for fabricating nanofibers.

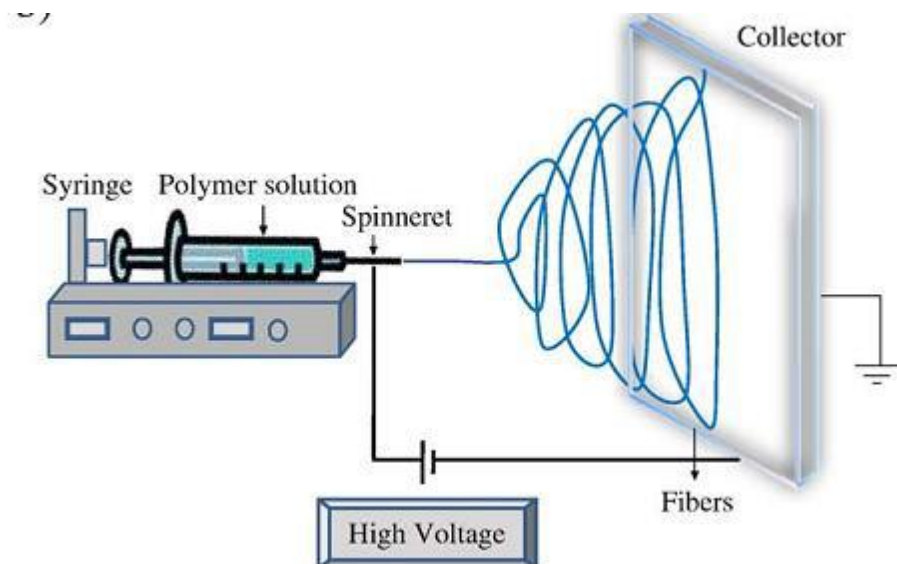
### **2.3.2. Methods of producing nanofibers**

A wide range of polymeric materials can be used for the fabrication of nanofibers. When the diameter of polymer fiber material is scaled down from micro to nano scale, several amazing and unique characteristics are observed. These fibers exhibit extremely high surface area to volume ratio, outstanding mechanical properties, high surface functionality and high porosity with exceptional pore interconnectivity. Some different methods have been used to fabricate nanoscale polymeric fibers, such as template synthesis (Ikegame, et al., 2003; Martin, 1996), drawing (Ondarcuhu and Joachim, 1998), self assembly (Feng et al., 2006; Yang and Xu, 2006), phase separation (Ma and Zhang, 1999), melt blowing (Ellison et al., 2007), and electrospinning (Formhals, 1934). Of all these nanofiber fabrication techniques, electrospinning is the easiest and fastest fabrication technique and therefore, the most promising technology for large scale production of nanofibers.



### 3. ELECTROSPINNING

Electrospinning, a word derived from “electrostatic spinning”, is a technology that has been recognized since the 1930’s. However, it did not gain much attention until the mid-1990s, when researchers realized the huge potential of this process for nanofiber fabrication (Zhou et al., 2003). A typical electrospinning setup (Figure 3.1) includes: a high-voltage power supply, a syringe, a metal needle, and a grounded collector. In electrospinning, a high voltage, usually larger than 5 kV, is applied to the solution. When the repulsive electrostatic forces between the charges on the drop surface overcome its surface tension, a jet is ejected from the drop. On its way to the collector, the jet bends and twists, and this cause the polymer to stretch (Rutledge and Fridrikh, 2007). Simultaneously, the solvent evaporates during this motion, leaving only solid polymer residues.



**Figure 3.1:**The electrospinning set up scheme (Bhardwaj ve Kundu, 2010).

In the past decade, over 50 polymers have been electrospun successfully, as reviewed by Huang et al (2003). However; many parameters affecting the results of electrospinning remain poorly understood. These parameters include: (1) the solution properties, such as concentration, viscosity, conductivity, and surface tension; (2)

operation variables, such as flow rate, operating voltage, the gap between the needle and the collector; and (3) electrospinning conditions, such as temperature and humidity (Huang et al., 2003; Kriegel et al., 2008; Pham, et al, 2006).

Among these parameters, the primary factor that influences the electrospinning process is the solution viscosity. As reported by Kriegel et al.(2008) and Pham et al. (2006) use of polymers with high molecular weight and solutions with significantly high concentration helps the nanofiber formation. However, highly concentrated (or viscous) solutions usually hinder the flow through the capillary, thus negatively affecting the process. For this reason, finding an optimal range of polymer concentrations is considered the most important step for successful electrospinning of nanofibers. Another important factor is the applied voltage. As mentioned previously, a jet can be produced if, and only if, the applied electrostatic force overcomes the droplet surface tension. At lower voltage, a pendant drop, usually sitting at the needle tip, cannot be detached from the tip. As the voltage increases, a thin jet starts to emerge and then exceeds a critical value (Deitzel et al., 2001). The applied voltage should be optimized during the electrospinning process. The fibers cannot be formed below a certain voltage because the repulsion force of the charged solution does not overcome the solution surface tension. In addition, although fibers can be formed above a critical voltage, they will usually contain bead defects (Deitzel et al., 2001).

In the electrospinning process, for fiber formation to occur, a minimum solution concentration is required. There should be an optimum solution concentration for the electrospinning process, as at low concentrations beads are formed instead of fibers and at high concentrations the formation of continuous fibers are prohibited because of the inability to maintain the flow of the solution at the tip of the needle resulting in the formation of larger fibers (Sukigara et al., 2003).

Surface tension has important effect on the electrospinning process. By reducing the surface tension of a nanofiber solution; fibers can be obtained without beads. Generally, the high surface tension of a solution inhibits the electrospinning process because of instability of the jets and the generation of sprayed droplets (Hohman et al., 2001). However, not necessarily a lower surface tension of a solvent will always be more suitable for electrospinning.



Solution viscosity plays an important role in determining the fiber size and morphology during spinning of polymeric fibers. It has been found that with very low viscosity there is no continuous fiber formation and with very high viscosity there is difficulty in the ejection of jets from polymer solution, thus there is a requirement of optimal viscosity for electrospinning (Sukigara et al., 2003).

It has been found that with the increase of electrical conductivity of the solution, there is a significant decrease in the diameter of the electrospun nanofibers whereas with low conductivity of the solution, there results insufficient elongation of a jet by electrical force to produce uniform fiber, and beads may also be observed (Hayati et al, 1987).

It has been already proved experimentally that the shape of the initiating drop changes with spinning conditions (voltage, viscosity, and feed rate) (Baumgarten, 1971).

In most cases, a higher voltage causes greater stretching of the solution due to the greater columbic forces in the jet as well as a stronger electric field and these effects lead to reduction in the fiber diameter and also rapid evaporation of solvent from the fibers results. At a higher voltage there is also greater probability of beads formation (Buchko et al., 1999; Deitzel et al., 2001; Demir et al., 2002; Megelski et al., 2002; Lee et al., 2004; Mo et al., 2004; Katti et al., 2004; Pawlowski et al., 2004; Haghi & Akbari, 2007).

The flow rate of the polymer from the syringe is an important process parameter as it influences the jet velocity and the material transfer rate. A lower feed rate is more desirable as the solvent will get enough time for evaporation (Yuan et al., 2004).

The tip and the collector distance is another method to control the fiber diameters and morphology. It has been found that a minimum distance is needed to give the fibers sufficient time to dry before reaching the collector, otherwise with distances that are either too close or too far, beads have been observed (Lee et al., 2004; Geng et al., 2005; Ki et al., 2005). The effect of tip and the collector distance on fiber morphology is not as significant as other parameters.

In general, natural polymers have better biocompatibility; therefore they are more ideal for human body, in comparison to synthetic alternatives. However, to transform a natural biopolymer into submicron or nanometer fibers via electrospinning is often

more difficult than to do a synthetic polymer. Due to this fact, only some literature have been discovered recently which report addressing electrospinning of some natural biopolymers (Jin et al, 2002; Wnek et al, 2003; Huang et al, 2003).

### **3.1 Characteristics of Electrospun Nanofibers**

Polymer nanofibers have a diameter in the order of a few nanometers to over 1  $\mu\text{m}$  (more typically 50–500 nm) and possess unique characteristics, such as: extraordinary high surface area per unit mass (for instance, nanofibers with ~100 nm diameter have a specific surface of ~1000  $\text{m}^2/\text{g}$ ), coupled with remarkable high porosity, excellent structural mechanical properties, high axial strength combined with extreme flexibility, low basis weight, and cost effectiveness, among others. Choice of the polymer solutions, co-processing of polymer mixtures, chemical cross linking of the formed nanofibers, etc, can provide a variety of pathways for controlling the chemical composition of electrospun nanofibers with a wide range of properties (such as strength, weight, elasticity, porosity, charged surface area, etc.). The electrospinning technique also provides the capacity to lace together a variety of types of nanoparticles or nanofillers to be encapsulated into an electrospun nanofiber matrix. Carbon nanotubes, ceramic nanoparticles, etc. may be dispersed in polymer solutions, which are then electrospun to form composites in the form of continuous nanofibers and nanofibrous assemblies. Various preparation techniques that allow the simultaneous introduction of specific functions into nanofibers have recently been developed (Frenot, 2003; Li and Xia, 2004; Jayaraman et al, 2004; T. Subbiah et al, 2005; Dersch et al, 2005). Electrospun nanofibers can furthermore be aligned to construct unique functional nanostructures, such as nanotubes and nanowires. Another interesting aspect of using nanofibers is that it is feasible to modify not only their morphology and their (internal bulk) content but also their surface structure to carry various functionalities (Deitzel et al, 2002; Bognitzki et al, 2000). Nanofibers can be easily post-synthetically functionalized (for example by chemical or physical vapour deposition). Furthermore, it is even feasible to control secondary structures of nanofibers in order to prepare nanofibers with core/sheath structures, nanofibers with hollow interiors and nanofibers with porous structures (Li and Xia, 2004). Overall, the main advantage of this top-down nanomanufacturing process is its relatively low cost compared to that of most bottom-up methods. The resulting nanofiber samples

are often uniform and continuous and do not require expensive purification (unlike submicrometer diameter whiskers, inorganic nanorods and carbon nanotubes) (Dzenis, 2004). Hence, polymer nanofibers mats are being considered for use in composite materials reinforcement, sensors, filtration, catalysis, protective clothing, biomedical applications (including wound dressing and scaffolds for tissue engineering, implants and membranes), space applications such as solar sails, and micro- and nanooptoelectronics (nanowires, LEDs, photocells, etc.). Carbon nanofibers made from polymeric precursors further expand the list of possible uses for electrospun nanofibers (Li and Xia, 2004; Jayaraman et al, 2004; Subbiah et al, 2005).

The characterization of electrospun fibers remains one of the difficult tasks as the chances of getting single fibers are rare (Bhardwaj & Kundu, 2010). Physical characterization of electrospun fibers is associated with structure and morphology of the sample. For morphological characterization, techniques such as scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) (Kriegel et al., 2009; Maretschek et al., 2008) and atomic force microscopy (AFM) are used (Bhardwaj & Kundu, 2010; Demir et al., 2002; Li et al., 2002). For chemical characterization of nanofibers, Fourier transform infra red (FTIR), nuclear magnetic resonance (NMR), circular dichroism (CD), differential scanning calorimetry (DSC), X-ray diffraction and X-ray scattering can be used. In some studies AFM tips and nano tensile testing systems were used for mechanical characterization (Bhardwaj & Kundu, 2010). The characterization studies should also include behaviors of electrospun nanofibers in dispersions, which may affect their utilization in foods.

The zeta potential is used for predicting and controlling the stability of colloidal suspensions or emulsions (Cho, Lee, & Frey, 2012). According to Kaasalainen et al. (2012), zeta potential has an important role in physical stability of nanosuspensions. A polymer spreads in the solution in time and this diffusion can be expressed by the Fick's law.

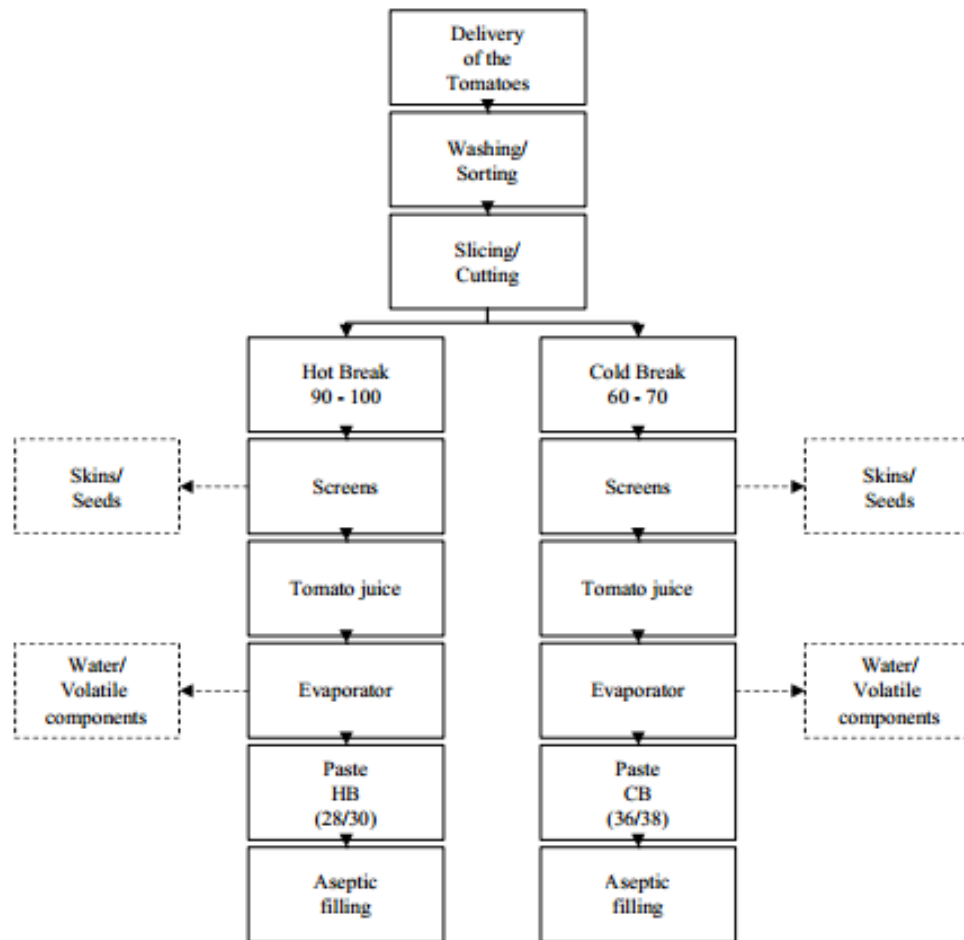
The diffusion coefficient,  $D$  (also known as diffusivity), can be determined using dynamic light scattering. It is linearly correlated with the mobility of the polymer (Doi and Edwards, 1986). Even though electrospinning is one of the "top-down"

approaches used in nanotechnology and does not change the structure of the molecule, the size-reduction to nanoscale may change some properties of the material. Gelatin can be considered as a polymer at bulk state, and its behaviors in dispersions may be evaluated using the polymer science. The diffusion coefficient and the mobility values may be taken into account for evaluating nanofibers in dispersions along with the influences of affecting parameters during electrospinning to design functionalities depending on their “job” in foods (Okutan N. et al., 2014).

#### **4. TOMATO KETCHUP**

Ketchup is a descriptive term for a number of different products, which consist of various pulp, strained and seasoned fruits; the variety made from tomatoes being the most popular condiment. Good quality ketchup is judged by flavour, consistency, uniformity and attractiveness of colour. Tomato ketchup is a clean, sound product made from properly prepared strained tomatoes with spices, salt, sugar and vinegar with or without starch, onions and garlic and contains not less than 12% of tomato solids. It is the most important product of tomato and is consumed extensively. A major part of the tomato processed is used for making ketchup (Gupta, 1998). Many newly developed tomato products with or without other vegetable juices are now appearing on the market, and among these new products with “high service content” tomato ketchups have been probably the first to find favour with the consumer and they still represent a large share of the market (Porretta and Birzi, 1995). Even though ketchup is known worldwide, information on this product in the technical/scientific literature is limited (Porretta, 1991) Commercial ketchup can have an extremely variable composition; nearly all manufacturers have a formula of their own which differs in some respects from those of other manufacturers. These differences are mainly in the quantity, number and amount of spices or other flavouring agents used. Thus, it is difficult to establish the analytical parameters on which quality depends. Usually viscosity is considered an important physical property related to the quality of food products. Viscometric data are also essential for the design evaluation of food processing equipment such as pumps, piping, heat exchangers, evaporators, sterilizers, filters and mixers (Koocheki et al., 2009).

Benner et al., (2007) described the ketchup manufacturing as follows; the tomatoes are processed into paste within one day from harvesting (Figure 4.1).

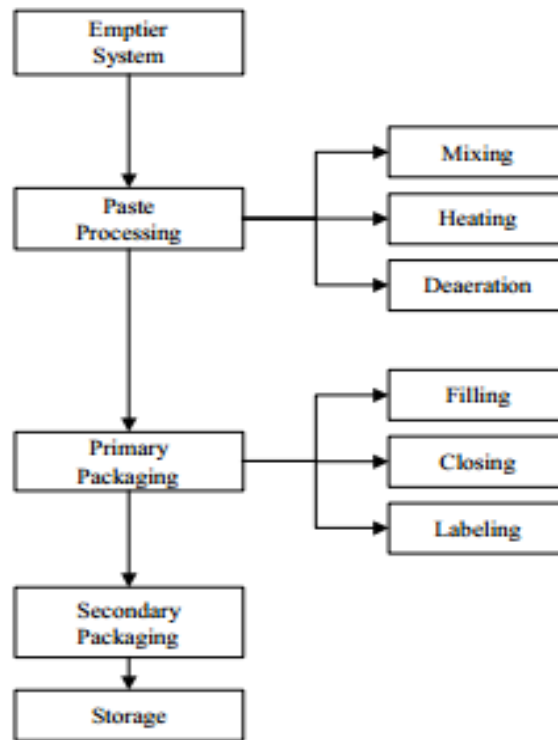


**Figure 4.1:** The production process of tomato paste (Benner et al., 2007).

At arrival at the paste plant, the tomatoes are washed and sorted. Only the red, ripe tomatoes are processed. Depending on the paste plant, the tomatoes are cut before further processing. Next, either a hot break (1 minute at 90 – 95 °C) or a cold break (1 minute at 70 °C) heat treatment is used. For the tomato ketchup production hot break paste is needed. Cold break paste is used for juices and vegetable cocktails. In cold break paste the pectolytic enzymes are activated, which subsequently destroy the cell walls. Cold break paste has a more natural colour and a fresher tomato taste. The product has a lower viscosity and is more susceptible to syneresis. Also more vitamin C is lost than in hot break paste (Gould, 1992; Hayes et al., 1998). Hot break paste has a higher viscosity, which is caused by the inactivation of all enzymes. The hot break process results in a higher yield with a higher consistency. The product is also less susceptible to syneresis (Gould, 1992; Hayes et al., 1998). After the hot or cold break process the tomato pulp is passed through screens to separate seeds and

peel and squeeze the juice out of the pulp. Next the juice is concentrated in an evaporator. Finally, the paste is packed in aseptic bags and transported to the production sites for tomato ketchup. After arrival at the ketchup production plant, ingredients are added to the paste. The paste with ingredients is heated, deaerated, filled, packed and stored.

The production process of tomato ketchup is shown in Figure 4.2.



**Figure 4.2:**The production process of tomato ketchup (Benner et al., 2007).

On the other hand McCarthy et al., (2008) described the manufacture of tomato by directly using tomato paste instead of beginning from the raw tomatoes. Tomato paste which have Brix in the range of 23-33 is the beginning constituent of the ketchup. Water is added to the tomato paste in order to dilute it, and adjust the soluble solid level. It is adjusted to the level of 16–19 Brix. Then the cooking process is occurred at 200°F (93°C). The other ingredients (such as salt, vinegar, sugar,

spices) are added again during this process. Finally the bottling of the product is achieved product and contains at least 12 percent tomato solids (Sharoba et al., 2005).

#### **4.1. Rheology of TomatoKetchup**

Rheology defines a relationship between the stress acting on a given material and the resulting deformation and/or flow that takes place. Therefore stress (force per area) and strain (deformation per length) are keys to all rheological evaluations. Stress ( $\sigma$ ) is a measurement of force per unit of surface area and is expressed in units of Pascals (Pa) and strain is a dimensionless quantity of relative deformation of a material.

The science of rheology has many applications in the fields of food acceptability, food processing, and food handling. Rheological measurements are quite relevant in the food industry as a tool for physical characterization of raw material prior to processing, for intermediate products during manufacturing, and for finished foods (Tabilo-Munizaga and Barbosa-Canovas, 2005).

Many foods of commercial importance, such as tomato paste and tomato ketchup, are concentrated dispersions of insoluble matter in aqueous media. Their rheological behaviour is important in the handling, storage, processing and transport of concentrated suspensions in industry (Rao ,1987) The viscosity of fluid foods is an important parameter of their texture. It determines to a great extent the overall feel in the mouth and influences the intensity of the flavour (Thomas et al., 1995). The yield point values of ketchup were correlated with the pectin content (Rani and Banins, 1987).

Ketchups are time-independent, non-Newtonian fluids that show a small thixotropy, which is a property in non-Newtonian liquids which causes return to their original viscosity only with a delay after the shear force stopped to act. (Bottiglieri et al., 1991).

The quality of ketchup is strongly dependent on its preservation. The most typical use of ketchup is in “fast-food” restaurants, where it is normally stored at room temperature after the opening of the container; the classic black ring which is formed in the bottle neck is a definite sign of the result of a Maillard-type degradation, which implies other important quality changes (Porretta and Birzi, 1995).



When time- independent material, e.g. ketchup, stirred or shaken, it becomes thinner and only returns to its original viscosity after allowing to rest for a while. Per definition, a thixotropic material does not only thin depending on the shear rate, but it additionally returns to its original viscosity after a material-specific period of rest. These gel-sol and sol-gel changes in thixotropic materials are reproducible (Steffe, 1996).

There are different models that can be used to define the rheological properties of tomato products (Smith, 2009; Bayod et al., 2007) under steady shear; for example, the Herschel–Bulkley, Casson (Bayod et al., 2007) and Ostwald de Waele (Smith, 2009) models. However, the data obtained shows variation as a result of different experimental conditions. Therefore it is difficult to obtain a general description about the rheology of tomato products (Bayod et al., 2007).

Like with the other tomato products tomato ketchup is studied within time and different models are suggested. The viscous properties of it have been traditionally described by a Power-Law model (Ostwald de Waele) or by models (Casson and Herschel-Bulkley) involving a yield stress value as a fitting parameter (Valencia et al., 2004).

The Ostwald de Waele (4.1) is given by;

$$\tau = K\dot{\gamma}^n \quad (4.1)$$

A general relationship to describe the behavior of non-Newtonian fluids is the Herschel-Bulkley models (4.2):

$$\tau = K(\dot{\gamma})^n + \tau_0 \quad (4.2)$$

Where  $\tau$  is the the shear stress (Pa),  $K$  is the flow consistency index ( $\text{Pa}\cdot\text{s}^n$ ),  $\dot{\gamma}$  is the shear rate ( $\text{s}^{-1}$ ),  $\tau_0$  is the yield stress (Pa), and  $n$  is the flow behavior index (dimensionless) (Steffe, 1996).

Fluids can be subdivided into three different types based on the value of their flow behaviour index, when  $n < 1$  the fluid is Pseudoplastic, when  $n = 1$  the fluid is Newtonian fluid and when  $n > 1$  the fluid is Dilatant which is less common (Anton et al., 2001).

The effect of different hydrocolloids on the rheological properties of tomato ketchup was studied by Koocheki et al. (2009). They reported that all the ketchup samples studied showed non-Newtonian, pseudoplastic behavior at different levels of hydrocolloids and at different temperatures. The Power-law and Herschel-Buckley are the models that were successfully fit to the data of shear stress versus shear rate. Varela et al., (2003) investigated the effects of xanthan gum and guar gum and also the effect of native corn starch on the rheology of tomato ketchup. They investigated the effects of them in some important properties such as serum separation and consistency of ketchup. They found that the Herschel-Bulkley is the suitable model to fit the experimental flow curves. The studies generally showed that the tomato ketchup is time-independent fluid. Some suggested that the ketchup can be described by pseudoplastic behavior but some characterized it as a thixotropic fluid (Varela et al., 2003).

#### **4.1.1. Tomato ketchup consistency versus viscosity**

Ketchup is a descriptive term for a number of different products, which consist of the pulp, strained and seasoned, of various fruits; the variety made from tomatoes being the most popular condiment. Good ketchup is judged by flavor, consistency, uniformity and attractiveness of color. Consistency/Viscosity is one of the most important quality parameters of tomato products (Vercet et al. 2002). The viscosity is defined in the standards of The United States' for semi solid products as the ability of the product to hold the liquid part in suspension (Tehrani and Ghandi, 2007). It affects the intensity of the flavour and it determines to a great extent the overall feel in the mouth (Sharoba et al. 2005). It is important from the engineering and consumer viewpoints (Rani and Bains, 1987). Therefore, reliable and accurate rheological data are necessary for designing and optimization of various unit operations (pumping, mixing, heating, etc.) and ensuring product acceptability since the products with improper consistency may be graded as unacceptable, or sold at a lower price. Tomato ketchup obtains its viscosity from naturally occurring pectic substances in fruits. Tomato varieties with less pectin may result in reduced consistency, and other factors such as enzymatic degradations, pectin/ protein interaction, pulp content, homogenization process and concentration may also affect the consistency of tomato

products (Crandall and Nelson, 1975; Stoforos and Reid, 1992; Tanglertpaibul and Rao, 1987).

However, the consistency can be maintained by adding polysaccharides such as starch, gum, etc. (Sidhu et al, 1997). There are few published articles about the effects of some hydrocolloids on the consistency of tomato ketchup processed directly from hot extracted tomatoes (Gujral et al, 2002; Sidhu et al, 1997). The product with a low consistency will result in two phases as pulp and serum that is the syneresis will actualize as a result of the inability of retaining the solid part in suspension (Krebbers et al, 2003).

Several parameters such as raw material quality and conditions for processing play an important role in the flow behavior of tomato ketchup. Therefore it is important to have a raw material with a satisfactory quality and to control and adjust the processing variables continuously to have a final product (ketchup) with a constant and desirable quality (Bayod et al., 2008). The syrup and the tomato fiber are the constituents of the tomato ketchup. The properties of the syrup, the ratio of syrup and tomato fiber are the principal factors that determine the consistency/viscosity of ketchup. The viscosity of the liquid and the proportion of insoluble tomato fiber present largely determine the thickness or body of the product. The variety and maturity of the tomatoes, the method of pulp preparation (hot break, cold break), the final pH of the finished products (Varela et al., 2003) enzymatic degradations, pulp network, pectin/protein interaction, homogenization process and concentration (Sahin and Ozdemir, 2004 ; Koocheki et al., 2009) are the other factors that affects the body. Consistency is of great importance, as consumers want their ketchup to be the same, bottle after bottle (Zonis, 2007).

Thick products are preferred by the consumers. Therefore nowadays thickeners are used in the tomato ketchup processing. To have a thick product, the manufacturers use tomato pulp powder (Farahnaky et al., 2008), potato or corn starches, modified starches or various hydrocolloids such as guar gum, carboxymethylcellulose (CMC), traganth gum, locust been gum, and xanthan gum (Panovská et al., 2009).

The consistency of tomato products depends on the amount of suspended particles (pulp) in a dispersing medium and is directly related to the tomato fruit constituents such as pectin. Other factors such as enzymatic degradations, pulp network,

homogenization process and concentration also play an important role in determining the consistency of tomato products (Valencia et al., 2003; Vercet et al., 2002).

Technological characteristics, such as chemical composition, rheological properties, physical properties and sensory properties play an important role in the formation of the processing steps, which are necessary for the production of tomato ketchup (Sharoba et al., 2005).

#### **4.1.2. Effect of hydrocolloids on ketchup rheology**

Tomato ketchup is a heterogenous suspension product, controlling of the phase separation in tomato ketchup is of a major commercial importance due to a high or low degree of serum separation during storage (Gujral et al, 2002; Stoforos and Reid, 1990).

Hydrocolloids are water-soluble, high molecular weight polysaccharides that find wide application in food industry because of their ability to improve the rheological and textural characteristics of food systems and often used as food additives for enhancing viscosity, creating gel-structures and lengthening the physical stability (Dickinson, 2003).

Sidhu et al. (1997) indicated that the consistency of tomato ketchup can be improved by adding polysaccharides such as gums. Gujral et al. (2002) reported that hydrocolloids increased the viscosity and reduced the serum loss of tomato ketchups. Also, Sahin and Ozdemir (2004) showed that all tested hydrocolloids can be used to improve consistency/viscosity of tomato ketchups.

Sahin and Ozdemir (2004) found that addition of LBG, tragacanth gum, guar gum and xanthan gum to ketchup resulted in greater shear thinning properties while CMC showed marginal effect. Consistency index and apparent viscosity increase with the addition of all hydrocolloids, but the increase is highest with the addition of guar and LBG, followed by xanthan and tragacanth and the least with CMC.

Sahin and Ozdemir (2007) investigated that both the addition of hydrocolloids, such as Tragacanth gum, guar gum, CMC, xanthan gum and locust bean gum (LBG), and increase in the amount of tomato paste in the formulation decreased the serum separation. However, the serum separation of ketchup samples was dramatically decreased by increasing the hydrocolloid concentration.

Koocheki et al. (2009) found that though guar gum produced higher apparent viscosity in tomato ketchup as compared to xanthan and CMC, the yield stress is higher for ketchups with xanthan and CMC but lower after addition of guar gum. Sidhu et al. (1997) indicated that the consistency of tomato ketchup can be improved by adding polysaccharides such as gums. Gujral et al. (2002) reported that hydrocolloids increased the viscosity and reduced the serum loss of tomato ketchups.

#### **4.1.3 Effect of temperature on ketchup rheology**

The ketchup is usually kept in the bottles outside of refrigerator in stores. Thus different temperatures might affect its rheological properties. This storage approach makes frequently results in a loss of ketchup consistency and serum separation, both of which are not accepted well by consumers. Hydrocolloids can be added to improve consistency and decrease the serum loss of the ketchup (Singh Gujral et al., 2002; Sahin and Ozdemir, 2007).

The viscosity is a function of temperature; when the temperature increases, there occurs an increase in intermolecular distances and the viscosity decreases (Sharoba et al., 2005).

Koocheki et al. (2009) studied on the rheological properties of ketchup as a function of temperature. They found in general that both consistency coefficients and yield point were significantly affected by temperature. They observed a decrease in consistency coefficients with the increase in temperature indicating a decrease in apparent viscosity at higher temperatures. Moreover they observed that ketchups tended to have higher pseudoplasticity at higher temperatures.

The relationship between effective viscosity and temperature for different brand ketchups was examined by Sharoba et al. (2005) and it was shown that effective viscosity values decreased as the temperature was increased. The effect of temperature on the viscosity was described with Arrhenius-type equation by Sharoba et al. (2005) and Koocheki et al. (2009).

$$K = A e^{-E_a/RT} \quad (4.3)$$

which K is rate constant ( $s^{-1}$ ), A is frequency factor,  $E_a$  is the energy of activation for viscosity ( $J mol^{-1}$ ), R is the universal gas constant ( $J mol^{-1} K$ ), and T is absolute temperature (K).

Moreover break step (hot or cold break) commonly used in the production ketchup and also in other tomato products are also indicative of the importance temperature. The tomatoes chopped are heated quickly to the temperatures of 60-77 °C for cold break and at least to 90° C for hot break (Chong et al., 2009). Hot break is used to produce products with high viscosity (Benner et al., 2007; Kuo- Chiang, 2008) such as ketchup and tomato sauce; on the other hand, the cold break method is used to produce products with lower viscosity values, such as juices (Chong et al., 2009; Kuo-Chiang, 2008). In cold break process the aim is to preserve the natural color and fresh flavor of the tomato; whereas, in hot break inactivating enzymes important to viscosity is the main objective. Hot break inactivates two enzymes, particularly endopolygalacturonase (EPG) and pectinmethylesterase (PME) (Kuo-Chiang, 2008). This contributes to the breakdown of pectin which is a polysaccharide found in the primary cell walls and middle lamella of higher plants ( Chong et al., 2009).

#### **4.1.4. Effect of pressure on ketchup rheology**

Several studies included some type of hydrocolloid to improve rheological properties of ketchup. However, another way to enhance consistency of ketchup is processing with valve homogenization. Generally, two stage, homogenization is utilized in industrial applications to produce glossy and smooth ketchup products. It improves overall ketchup quality by breaking up the fibrous tomato structure and reducing average particle size (Thakur et al., 1995; Bayod and Tornberg, 2011; Bayod et al., 2007). In conventional homogenization the ketchup is forced through a microscopic opening in the homogenizing valve. This creates high turbulence and shear, combined with compression, acceleration, pressure drop, cavitations, and impact. Consequently, disintegration and dispersion of the tomato solids throughout the ketchup take place.

Based on Kuo-Chiang Hsu et al. (2008) study processing in high pressure improves both viscosity and color properties when compared with their conventional heat processing counterparts.

Thakur et al., (1995) investigated how homogenization pressure affects the consistency of tomato juice and found that when tomato juice was homogenized under pressure at room temperature, the consistency increased and the serum separation decreased.

Krebbers et al., (2003) investigated how the viscosity is affected by combined high-pressure thermal treatments and they stated that at ambient temperature high pressure processing resulted with improved viscosity and color compared to heat pasteurization. They claimed that the adverse quality effects of hot-break step (in hot break there is a loss in quality in terms of color, flavor, and nutritional value) can be avoided by high-pressure processing.

#### **4.2. Syneresis in Ketchup**

Syneresis, the separation of liquid from a gel, is a common problem with some foods. Without proper control or preventative measure, syneresis could result in significant loss of moisture, flavor, color, and eventually the quality of food (Glicksman, 1977; Hoefler, 2004). Serum separation or syneresis is one of the most important problems in processed tomato products and it affects both product quality and hence consumer acceptability negatively. The problem can be reduced by using hot-break processing techniques and a partial removal of excess serum by centrifugal decantation (Porretta et al., 1995). Den Ouden and Van Vliet (2002) reported that serum separation of tomato suspensions is probably caused by uniaxial compression of the network under its own weight. Since tomato ketchup is a heterogenous suspension product, controlling of the phase separation in tomato ketchup is of a major commercial importance due to a high or low degree of serum separation during storage (Gujral et al., 2002; Stoforos and Reid, 1990). Quantitative studies have been carried out to predict the serum separation of tomato products and researchers have tried to find a relationship between serum separation potential of ketchup and blotter test, Bostwick flow value, gravity sedimentation test etc. It has been researched that, by proper blending of hydrocolloids, the degree of syneresis could either be reduced or delayed (Imeson 2000; Hoefler 2004). Sidhu et al. (1997) indicated that the consistency of tomato ketchup can be improved by adding polysaccharides such as gums and Gujral et al. (2002) reported that hydrocolloids increased the viscosity and reduced the serum loss of tomato ketchups. Hydrocolloids find wide application in food industry because of their ability to improve the rheological and textural characteristics of food systems and often used as food additives for enhancing viscosity, creating gel-structures and lengthening the physical stability. (Dziezak, 1991; Glicksman, 1991; Garti and Reichman, 1993; Dickinson, 2003; Hinrichs and Weisser, 2003). Several

processing parameters (direct syneresis factors) such as time, temperature, agitation, size of particles, and volume of liquid surrounding the particles all affect the syneresis rate (Lawrence, 1959a,b).



## 5. HYDROCOLLOIDS

Hydrocolloids are defined as “a macromolecular substance such as a protein or polysaccharide which swells by absorption of water, in some cases forming a stiff gel” (Ockerman, 1978). Food hydrocolloids, or food gums, have high molecular weights when compared to carbohydrate ingredients, such as sugar or corn syrup (Hegenbart, 1993). Food gums are usually added to food systems/products for specific purposes, such as thickening agents, stabilizers, emulsifiers, gelling, etc (Kuntz, 1999; Hoefler, 2001). Hydrocolloids ultimately alter the rheological properties in a desired fashion for food systems (Pedersen, 1979).

The typical structure of a food hydrocolloid includes a sugar backbone with protruding substituents (Kuntz, 2002). The backbone can vary in length from several hundred to several thousand sugar units long (Kuntz, 1999). These sugar units are most commonly linear in form, but branched backbones have been seen. The backbone provides pertinent information such as the acid stability of the particular hydrocolloid. The type, number, and distribution of substituents protruding from the backbone determine whether a gum is a thickening agent or a gelling agent (Hegenbart, 1993).

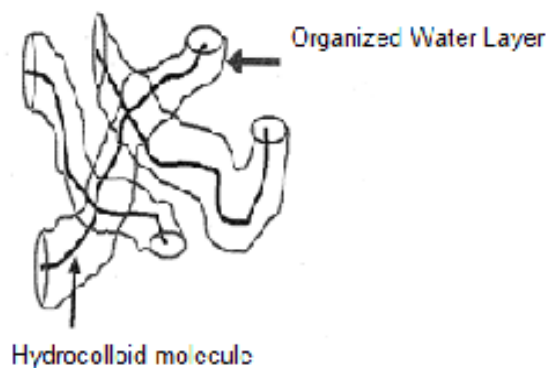
Origin of the commercially important hydrocolloids is given in Table 5.1. Most of the hydrocolloids are found naturally, but some such as CMC are obtained after some chemical modifications.

**Table 5.1:** Source of commercially important hydrocolloids. (Philips and Williams,2000).

<b>Botanical</b>	<b>Algal</b>	<b>Microbial</b>	<b>Animal</b>
Trees (cellulose)	Red seaweeds (Agar, carrageenan)	Xanthan gum	Gelatin
Tree gum exudates ( gum arabic, gum karaya, gum ghatti, gum tragacanth)	Brown seaweeds (Alginate)	Curdlan	Caseinate
Plants (starch, pectin, cellulose)		Dextran	Whey protein
Seeds (guar gum, locust bean gum, tara gum, tamarind gum)		Gellan gum	Chitosan
Tubers (konjac manan)		Cellulose	

## 5.1 Some Important Properties of Hydrocolloids

Chemical or physical structures of hydrocolloids show variation; while some, such as pectin and cellulose, have linear structure, some have branched molecules. Some are soluble in cold water while some only in hot water. Some, such as cellulose, are not digestible. Most of the hydrocolloids have side units (mostly sugar units, or sometimes carboxyl groups, sulfate groups or methyl ether group) which influence the properties of the hydrocolloid. Water molecules are oriented around hydroxyl groups of sugar units (and around anionic groups presenting on some gums) and moves around with the gum molecule to some extent leading to volume increasing and swelling (Figure 5.1). Some gum (namely thickeners) molecules exhibit little interaction with each other, moving with their layer of organized water following them. Some gum (namely the gelling agents) molecules make interactions with each other, using various types of bonds, forming a threedimensional network called a gel (Hoefler, 2004).



**Figure 5.1 :** Hydrocolloid molecules surrounded by organized water (Hoefler, 2004).

## 5.2. Functions

As stated previously, hydrocolloids are added to various food systems for a variety of reasons. Listed below in Table 5.2 are some of the functions of hydrocolloids along with the types of foods they are used in. However, there is usually one of three reasons why they are added to any food product. Those reasons are to influence the texture, to increase the stability, or to reduce fat or calories in a food product.

**Table 5.2:** Functions and applications of commonly used hydrocolloids (Stephen et al., 2006).

Hydrocolloid	Function	Application
Guar and locust bean gums	Stabilizer, Water retention	Dairy, ice cream, dessert, bakery
Carrageenans	Stabilizer, thickener, gelation	Ice cream, meat products, dressings, instant puddings
Agars	Gelation	Dairy, confectionery, meat products
Gum arabic	Stabilizer, thickener, emulsifier, encapsulating agent	Confectionery, bakery, beverages, sauces
Gum tragacanth	Stabilizer, thickener, emulsifier	Dairy, dressing, confectionery, sauces
Pectins	Gelation, thickener, stabilizer	Jams, preserves, beverages, confectionery, dairy
Alginates	Stabilizer, gelation	Dressings, beverages, dairy, bakery
Xanthan gum	Stabilizer, thickener	Dressings, beverages, dairy, bakery
CMC	Stabilizer, thickener, water retention	Ice cream, batters, syrups, cake mixers, meats
Methyl cellulose	Gelation, stabilizer, water retention	Fat reducer, bakery
Modified starches	Stabilizer, emulsifiers	Bakery, soups, confectionery

### **5.2.1. Viscosity enhancing or thickening function of hydrocolloids**

The foremost reason behind the ample use of hydrocolloids in foods is their ability to modify the rheology of food system. The modification of texture and/or viscosity of food system helps to modify its sensory properties, and hence, hydrocolloids are used as important food additives to perform specific purposes. The process of thickening involves nonspecific entanglement of conformationally disordered polymer chains; it is essentially polymer-solvent interaction (Philips et al., 1986). The thickening effect of produced by the hydrocolloids depends on the type of hydrocolloid used, its concentration, the food system in which it is used and also the pH of the food system and temperature. Ketchup is one of the most common food items where the hydrocolloid thickeners are used to influence its viscosity (Sahin & Ozdemir, 2004).

The question that arises is how hydrocolloids thicken solution. In dilute dispersion, the individual molecules of hydrocolloids can move freely and do not exhibit thickening. In concentrated system, these molecules begin to come into contact with one another; thus, the movement of molecules becomes restricted. The transition from free moving molecules to an entangled network is the process of thickening. The viscosity of polymer solutions is influenced significantly by the polymer molecular mass. In addition to molecular mass effects, the hydrodynamic size of polymer molecules in solution is significantly influenced by molecular structure. Linear, stiff molecules have a larger hydrodynamic size than highly branched, highly flexible polymers of the same molecular mass and hence give rise to a much higher viscosity (Url-8).

### **5.3. Gelatin**

Gelatin is a water soluble biopolymer derived from thermal denaturation of collagen. Being the most abundant protein constituent in the vertebrate body, collagen is distributed within animal skins, bones, tendons and vessels (Brinckmann, 2005).

Its manufacture involves the conversion of the collagen present in these tissues and the removal of the non-collagen materials present in the material (Johns and Courts, 1977).

Since all gelatins are derived from collagen it is pertinent to describe the structure of these macromolecules before discussing gelatin. The collagen monomer (tropocollagen) is a triple helical rod made up of three parallel chains. The collagen molecule is about 300 nm long, 1.5 nm in diameter and with a molecular weight around 300,000 Da (Dalton). On gelatin manufacturing, the collagen molecule unfolds into a mixture of chains and described above. The amino acid composition of these chains is quite unique and the three-chains involved in a collagen molecule may have slightly different amino acid compositions. The general amino acid sequence is Gly $\pm$ X $\pm$ Y, where X often is proline and Y often is hydroxyproline. This means that glycine accounts for about one-third of all the residues in collagen and gelatin. Sulphur-containing amino acids are virtually absent and the crosslinks between the chains do per se not involve these types of residue. (Phillips et al., 2000) Collagen is completely insoluble in water but small fractions are soluble in dilute acid or salt solution. The collagen solubility will, however, decrease as a result of the ageing processes occurring in most mammals. This is due to an increasing number of intra- and intermolecular covalent linkages which are formed in the source tissue upon ageing. It is the stable intra- and intermolecular crosslinks that require the use of severe processing to obtain soluble gelatins, which in turn leads to a polydisperse molecular weight distribution. Type A gelatins have more or less identical amino acid compositions to their parent collagen and the average isoelectric point of type A gelatins are therefore similar to collagen and in the range 7 $\pm$ 9.4. One exception to this is type A bovine hide gelatins which have a lower isoelectric point in the range 5.7 $\pm$ 7.4 due to specific pre-treatments. Type B gelatins lack many of the non-ionizable glutamine and asparagine residues because these amino acids are converted into their carboxyl forms by alkali deamination and the gelatins become more acidic. Thus the average isoelectric points of alkali processed gelatins are lower and in the range 4.8 $\pm$ 5.5.

The gelatin and collagen -chains consist of polar and non-polar regions. The 'non-polar' regions are made up from the tripeptide Gly-Pro-R, where R is a non-polar amino acid, predominantly hydroxyproline. These 'non-polar' regions are interspersed with polar regions, which are relatively deficient in both proline and hydroxyproline. The presence and distribution of the charged, polar and non-polar amino acids provides gelatin with unique properties. Gelatin is easily dissolved in water at the right conditions due to the presence of charged amino acids and forms

colloidal solutions. This means that gelatin by definition is a hydrocolloid. Due to its chemistry, gelatin is a multifunctional hydrocolloid with considerable surface activity (Phillips et al., 2000).

All types of gelatin have similar compositions, which contain water, small amount of mineral salts and pure protein from the connective tissue. However, depending on the material used, the pre-treatment process employed and the intensity of hydrolysis, several types of gelatin with different properties can be obtained (Schott, 2001).

According to Johnston-Banks (1990), the gelatin properties are significantly influenced by two main factors: the characteristics of the initial collagen and the extraction process. The gelling properties of gelatins are strongly influenced by the origin of the raw material used in the process due to the different proline and hydroxy proline contents in the collagen of the various species, which are associated with temperature and habitat of the animal (Kolodziejska et al., 2003). The extraction process is of fundamental importance as it is the determining factor for the molecular weight distribution of gelatin (Muyonga et al., 2004), the differences in the levels of collagen components (chains  $\alpha$ ,  $\beta$  and  $\gamma$ ) and the ratio between chains  $\alpha 1$  and  $\alpha 2$ , which influence the gelatin behavior (Jongjareonrak et al., 2010; Montero et al., 2002).

Commercially, skins or bones of different animal species, such as beef, pork, fish and poultry, form the main raw material for gelatin production. The extracted gelatin is a group of molecules of different molecular weight. The molecular weight profile depends on the process. The amino acid profile determines hydrogen bond formation and reactivity via side groups such as amine, imidazole, alcohol, amide and carboxylic acid. It hydrates readily in warm or hot water to give low viscosity solutions that have good whipping and foaming properties. After cooling, the network of polypeptide chains associates slowly to form clear, elastic gels that are syneresis free (Imenson, 2010).

In the manufacturing of gelatin, raw materials are pretreated with either acid or alkaline to allow the swelling of collagen in order to increase the efficiency of gelatin extraction during thermal hydrolysis. The resultant gelatin may be classified into two types: Acid pretreated gelatin is classified as Type A gelatin with an isoelectric point between 7 and 9; and alkali pretreated gelatin as Type B gelatin with

an isoelectric point of about 5 (Eastoe and Leach, 1977). Pretreatment with a mild acid does not hydrolyze the amide nitrogen of glutamine and asparagine, thus, yielding type A gelatin with an isoelectric point that might be as high as 9.4. If a more severe acid solvent is used during the pretreatment process, the isoelectric point of the resulting gelatin ranges from 6 to 8, which is similar to that of a collagen molecule in the raw material (Eastoe and Leach, 1977). In alkaline pretreatment process, the alkali progressively hydrolyses the amide groups of asparagine and glutamine side chains of collagen leading to a reduction in the number of amide groups. As a result, there is a net negative charge on the collagen molecule due to number of carboxyl groups remaining on gelatin molecule, thus resulting in a lower isoelectric point (Malafaya et al., 2007; Young et al., 2005).

The classical food, photographic, cosmetic and pharmaceutical application of gelatin is based mainly on its gel-forming and viscoelastic properties. Recently, and especially in the food industry, an increasing number of new applications have been found for gelatin in products such as emulsifiers, foaming agents, colloid stabilizers, fining agents, biodegradable packaging materials and micro-encapsulating agents, in line with the growing trend to replace synthetic agents with more natural ones. Moreover, in many cases, these studies are dedicated to using collagens and gelatins from alternative sources to land-based animals (Gómez-Guillén, 2011).

Gelatin formulations in the food industry use almost exclusively water or aqueous polyhydric alcohols as solvents for candy, marshmallow, or dessert preparations. In dairy products and frozen foods, gelatin's protective colloid property prevents crystallization of ice and sugar. Gelatin products having a wide range of Bloom (gel strength) and viscosity values are utilized in the manufacture of food products, specific properties being selected depending on the needs of the application. For example, a 250-Bloom gelatin may be utilized at concentrations ranging from 0.25% in frozen pies to 0.5% in ice cream; the use of gelatin in ice cream has greatly diminished. In sour cream and cottage cheese, gelatin inhibits water separation, that is, syneresis. Marshmallows contain as much as 1.5% gelatin to restrain the crystallization of sugar, thereby keeping the marshmallows soft and plastic; gelatin also increases viscosity and stabilizes the foam in the manufacturing process. Many lozenges, wafers, and candy coatings contain up to 1% gelatin. In these instances, gelatin decreases the dissolution rate. In meat products, such as canned hams, various



luncheon meats, corned beef, chicken rolls, jellied beef, and other similar products, gelatin in 1–5% concentration helps to retain the natural juices and enhance texture and flavor. Use of gelatin to form soft, chewy candies, so-called gummy candies, has increased worldwide gelatin demand significantly. Gelatin has also found new uses as an emulsifier and extender in the production of reduced-fat margarine products. The largest use of edible gelatin in the United States, however, is in the preparation of gelatin desserts in 1.5–2.5% concentrations. For this use, gelatin is sold either premixed with sugar and flavorings or as unflavored gelatin packets. Most edible gelatin is type A, but type B is also used (Seidel, 2008).

### **5.3.1. Electrospinning of gelatin**

The first important step in electrospinning a natural polymer is the preparation of an electrospinnable solution using a proper solvent. Water is a good solvent of gelatin because it breaks very easy the interchain links and produces stable solutions at 50°C, without gelatin degradation. However, gelatin/water system cannot be processed with electrospinning. Moreover, when dissolved in water at a temperature around or above 37-8 ° C, gelatin becomes a kind of a colloidal sol and hence without a special treatment (e.g., cross-linking) is not suitable for application. However, gelatin does have an important merit that it is a cheap biopolymer. By some post treatment or mixed with another (synthetic) biodegradable polymer (Giusti et al, 1997.), gelatin can be used alone or as a blend component to prepare nanofibrous membranes for various applications.

Because of these limitations in using water as a solvent, electrospinning of gelatin requires the use of fast evaporating organic solvents. Formamide, dimethyl sulphoxide and 2-chloroethanol were used because they prevent helix formation (Kozlov et al., 1983). Fluorinated alcohol solvents such as trifluoroethanol and hexafluoro isopropanol were found also to be good solvents for polypeptides (Gast et al., 2001). The formic acid was found to produce gelatin solutions suitable for electrospinning experiments. Solutions of 7-12% (w/v) gelatin dissolved in formic acid were successfully electrospun into nanofibers with diameters in the range from 70 nm to 170 nm (Ki et al., 2005). But, in time, the formic acid determines gelatin degradation and an important decrease of the solution viscosity, which makes the electrospinning process impossible due to beads formation (Ki et al., 2005). Another

example of highly polar, hydrogen-bonding organic solvents in which gelatin dissolves is acetic acid (Finch et al., 1997).

The second important problem in gelatin electrospinning is the gelatin concentration of the electrospinnable solution. It was reported that gelatin solutions with gelatin concentrations higher than 12% could not be electrospun because a hardened gelatin phase developed on the edge of the needle tip, disturbing the fluid filament flow and the quality of the resulted nanofibers (Huang et al., 2004). However, electrospinning of high concentration gelatin solutions is desirable, because the initial gelatin concentration was shown to be the most important parameter in controlling the cross-linking density and cytotoxin formation in gelatin biomedical applications (Montenegro et al., 2003; Landfester, 2003).

#### **5.4. Cellulose Acetate (CA)**

Cellulose, the most abundant natural polymer, is used traditionally in the paper making industry. CA is a semi synthetic polymer obtained from esterification of highly pure cellulose with acetic anhydride using sulfuric acid as a catalyst. Its properties depend on the esterification degree (degree of substitution) defined by the number of OH groups substituted by acetate groups which in turn defines the obtained material as acetate, diacetate or triacetate (Schilling et al., 2010). This cellulose derivative has partially or completely acetylated (COCH<sub>3</sub>) hydroxyl groups. Cellulose acetate is available in a wide range of acetyl levels (29-44.8%) and chain lengths, with molecular weights ranging from 30 000 to 60 000 (Rowe, 2009).

The properties of CA include low weathering, heat and chemical resistance, thermal stability, reasonable toughness and dimensional stability (Brydson, 1999). The most common form of CA fiber has an acetate group on approximately 2–2,5 of every three hydroxyls. This cellulose diacetate is known as secondary acetate, or simply as “acetate” (Fischer et al., 2008).

These properties make CA very attractive in semi-permeable membranes for dialysis, ultra filtration and reverse osmosis (Edgar et al., 2001). Traditional raw materials for the manufacture of CA include renewable, biodegradable, and inexpensive wood pulp. However alternative sources have also been considered, including residues

from sugar cane bagasse (Alves et al., 2008; Meireles et al., 2008), bacterial cellulose (Barud et al., 2008), newspapers (Rodrigues et al., 2008) and fruit seeds (Meireles et al., 2010).

In addition, according to generally recognized as safe (GRAS) materials, by food and drug administration (FDA), CA can be used in food products (Url-9).

#### **5.4.1. Electrospinning of cellulose acetate**

The use of cellulose and its derivatives to obtain nano-fibers by the electrospinning process presents a great opportunity for better utilization of cellulose and development of new applications (Frey, 2008). However, processing via electrospinning of biopolymers such as cellulose usually present challenges. This is due to their limited solubility in typical solvents and their tendency to aggregate or form gels (Kriegel et al., 2008). Successful efforts to electrospin cellulose report a process with typical low efficiency, yielding low amounts of material in a relatively long time (Kim et al., 2006). Few solvents are capable of dissolving cellulose so that it can easily be processed by electrospinning. Among those N-methylmorpholine (NMMO) / water (Turbak et al., 1981), lithiumchloride/N,N-dimethylacetamide (Kim et al., 2005), and ionic liquids such as 1-allyl-3-methylimidazolium chloride (AMIMCl) / dimethylsulfoxide (DMSO) (Xu et al., 2008) have been reported. The problem faced with such solvents is their low volatility which leads to defective fibers upon spinning. Additionally, some of these solvents require high temperatures to completely dissolve cellulose, making the processing even more difficult. On the other hand, it is reported that residual ions are difficult to remove from the obtained fibers (Huang et al., 2003; Lee et al., 2009).

Electrospinning of cellulose can be facilitated by using cellulose esters solutions followed by regeneration (Lee et al., 2009). For example, CA can be easily dissolved and processed in non-polar solvents, suitable for electrospinning such as acetone, dichloromethane, chloroform and methyl acetate (Zhang et al., 2008). As an alternative to the direct electrospinning of cellulose solution, the electrospinning and subsequent deacetylation of CA has been studied using various solvent systems (Liu et al., 2002; Son et al., 2004; Ma et al., 2005). Liu and Hsieh (2002) studied the relationships between the properties of the CA solutions and the structure of the electrospun fibers using acetone, acetic acid, N,N-dimethylacetamide (DMAc), and

their mixtures. They concluded that a mixed solvent of acetone/DMAc (2:1) was the most versatile solvent for the electrospinning of CA. In Son et al. Study (2004), CA nanofibers were continuously electrospinning a mixed solvent of acetone/water at water contents in the range of 10–15 wt.%.

### **5.5. Hypothesis**

In this study the first hypothesis is using different electrospinning process parameters to study the effect of them on morphology, zeta potential and diffusion coefficient of nanofiber. Secondly, in this study, it has been hypothesized that electrospun nanofibers of gelatin or gelatin-CA may inhibit the syneresis in tomato ketchup.

## **6. MATERIALS AND METHODS**

### **6.1 Material**

For tomato ketchup preparation, cold-break, double concentrated tomato paste having a total soluble solids (TSS) content of 28–30%, with ingredients typically used in ketchup preparation (sugar, salt and apple vinegar), and commercial tomato ketchup (Tamek) were purchased from local markets in Istanbul, Turkey. Xanthan gum (Neimenggu Fufeng Biotechnologies Co. LTD, NH110708014, China), inulin (USA), pectin (Seyidođlu, Turkey), CMC (Acıpayam Selüloz Sanayii ve Tic. Co., Turkey), glacial acetic acid, type B gelatin powder from bovine skin, CA (Sigma-Aldrich), and ethanol (AYS Ltd. Şti., Turkey) were also purchased.

### **6.2 Method**

#### **6.2.1 Preparation of feed solutions**

Concentration of solutions and their preparation to feed in electrospinning device are given in table 6.1 .

#### **6.2.2 Measurement of the electrical conductivity of solutions**

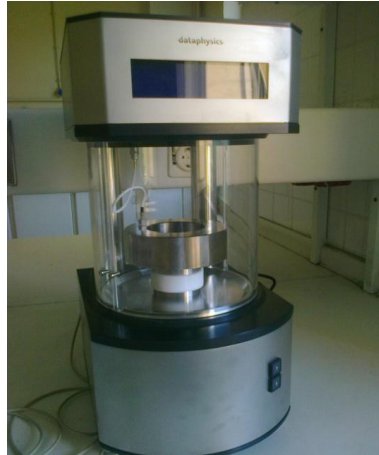
The electrical conductivities of feed solutions were measured using a conductometer (WTW LF95, Germany) at room temperature in duplicate.

**Table 6.1:** Solution preparation for electrospinning.

Polymer	Co-polymer	Blend ratio (v/v)	Solvent For polymers	Solvent blend ratio (v/v)	Stirring time ( hr)	Stirring temperature (°C)
Gelatin 7%	-	-	Acetic acid- Water	(50:50)	6	40
Gelatin 20%	-	-	Acetic acid- Water	(50:50)	6	40
Gelatin 10%	-	-	Acetic acid- Water	(90:10)	6	40
CA 17%	-	-	Acetic acid- Water	(75:25)	8	40
CA 10%	-	-	Acetic acid- Water	(75:25)	8	40
Pectin 2%	-	-	Water	-	2	Room temp.
Pectin 3%	-	-	Water	-	2	Room temp.
Xanthan gum 0.2%	-	-	Acetic acid- Water	(50:50)	-	-
Inulin 5%	-	-	Water	-	1	30
CMC 2%	-	-	Acetic acid- Water	(50:50)	12	50
CMC 3%	-	-	Acetic acid- Water	(50:50)	12	50
CA 2%	-	-	Acetic acid- Water	(50:50)	8	40
CA 3%	-	-	Acetic acid- Water	(50:50)	8	40
Pectin 2%	Gelatin 10%	(1:2)	-	-	12	30
Pectin 2%	Gelatin 10%	(1:5)	-	-	12	30
Pectin 3%	Gelatin 10%	(1:2)	-	-	12	30
Pectin 3%	Gelatin 10%	(1:5)	-	-	12	30
CMC 2%	Gelatin 20%	(1:3)	-	-	12	30
CMC 3%	Gelatin 20%	(1:3)	-	-	12	30
CA 2%	Gelatin 20%	(1:3)	-	-	12	30
CA 3%	Gelatin 20%	(1:3)	-	-	12	30
CA 17%	Gelatin 10%	(1:3)	-	-	12	30

### 6.2.3 Determination of surface tension of solutions

The surface tensions of feed solutions are measured by tensiometer (Dataphysics DCAT 11EC, Germany) (Figure 6.1) at ambient temperature by using Wilhelmy Plate technique in duplicate. The results are analyzed by SCAT Dataphysics (Germany) software.



**Figure 6.1:** Tensiometer setup (Dataphysics DCAT 11EC, Germany).

### 6.2.4 Rheological properties of feed solutions

The rheological characterization of feed solutions were determined with (HAAKE Rheostress 1, Germany) at 25° C, in the shear rate range of 0 to 200 s<sup>-1</sup> in 120 s and a parallel plate sensor (diameter = 35 mm, gap = 1 mm), with two replicates (Figure 6.2).



**Figure 6.2:** Rheometer setup (HAAKE Rheostress 1, Germany).

The results were modeled using the software (Haake RheoWin3 Data Manager, Germany) according to the power-law equation (4.1), and Herschel-Bulkley equation (4.2).

### 6.2.5. Electrospinning

The electrospinning process was carried out using with the equipment (Inovenso NE100, Turkey) at room temperature(Figure 6.3). The electrospinning device was fed by prepared solution for obtaining nanofibers. Different voltages (25- 35kV), solution flow rates(0.1-3 ml / h), and the tip to target distance (5-15cm) were applied in electrospinning process.



**Figure 6.3:**Electrospinning setup (Inovenso NE100, Turkey).

### 6.2.6. Scanning Electron Microscopy (SEM)

Diameters and morphological properties of the obtained nanofibers were investigated by using a Field Emission Scanning Electron Microscopy (FESEM) (JEOL, Japan). The samples are given Table 6.2.



**Table 6.2:** Samples for FESEM characterization.<sup>a</sup>

Sample	Blend ratio (v/v)	Applied voltage (kV)	Flow rate (ml/h)	The amount of obtained nanofiber (mg) <sup>b</sup>
Gelatin 7%	-	28	1	13.67
Gelatin 20%	-	28	1	33.33
Gelatin 20%	-	35	1	22.35
Gelatin 10% + CA 17%	(3:1)	40	1	4.5
Gelatin 10% + CA 17%	(3:1)	20	1	1.8
Gelatin 10% + CA 17%	(3:1)	40	6	2

a. In all samples, collector plate distance is 10 cm and the nanofiber obtaining time is 10 min.

b. It is theoretical calculation for the total amount of fibers

### 6.2.7 Zeta Potential and Diffusion Coefficient

The zeta potential and translational diffusion coefficient measurements of electrospun samples were carried out using a dynamic light scattering instrument (Malvern Zetasizer Nano ZS, Worcestershire, UK) at 25° C in duplicate (Figure 6.4).



**Figure 6.4:** Zetasizer setup (Malvern Zetasizer Nano ZS, Worcestershire, UK).

Ethanol was used as a dispersant for all samples during both measurements, because fibers did not dissolve in ethanol. Sample was dispersed at 0.1% (w/v) in ethanol. After 10 min electrospinning the amount of electrospun gelatin samples collected on the plate were found by taking the concentration of the feed solution and the feed rates into account.

### 6.2.8. Ketchup preparation

Ketchup samples were prepared according to the constituents below:

1- tomatopaste (44% wt)

2- sugar (8.3 % wt)

3- vinegar (8.3 %wt)

4- salt (7% wt)

5- water (38% wt).

The tomato paste and water were mixed, then the mixture was heated on a hot plate, set at a moderate temperature, and stirred constantly until the mixture reached a temperature between 75 and 80 °C. At this point, sugar and salt were added, and mixed with blender (Tefal, France), and heating was continued until the mixture attained a TSS content of 25% . The TSS measured by using refractometer (RL3, Poland ). Then, apple vinegar was added to the mixture, and the ketchup was heated until a TSS of 26.5% was obtained. Finally the ketchup was immediately portioned into three samples of 1 kg each. The nanofibers were then added into each 80 gr of ketchup, at different levels. The gelatin nanofiber were added into ketchup at level of 0.25% and 0.5%, and gelatin-CA added into ketchup at level of 0.5%, and stirred for 2 min at 5000 rpm with an blender. Each sample was then immediately poured into the glass tubes, while still hot, and then stored at two different temperature (4 and 25°C) (Sahin and Ozdemir, 2007). The addition of nanofibers containing gelatin-CA to ketchup was only at 0.5% and these samples were stored only for one week. This is due to fact that electrospinning from the blend of gelatin and CA was hard and taking time process, approximately less than 1 mg nanofiber is obtained after one day electrospinning. Moreover, firstly the addition of electrospun gelatin nanofibers on rheology of ketchup was studied and results indicated that most stabile ketchup samples were the ones that were kept at 4 °C, including stability of samples did not drastically change after one week. Therefore, electrospun nanofibers containing gelatin-CA were added to ketchup at 0.5% and these samples were kept at 4 °C

### **6.2.9 Rheological properties of ketchup samples**

The rheological characterization of ketchup samples were determined with the same method mentioend in section 6.2.4, in the shear rate range of 0 to 300 s<sup>-1</sup> in 120 s.

### 6.2.10 Serum separation measurement

Serum separation of ketchup samples were determined by centrifuge (3-16 L Sigma, Germany). (Figure6.5)



**Figure 6.5:** Centrifuge setup (3-16 L Sigma, Germany).

A measured amount of ketchup was taken in a centrifuge tube and centrifuged at 2200 and 5000g respectively, at 20°C for 10 min (Sahin and Ozdemir, 2007). The supernatant was discarded and the remaining part was weighed. The serum separation was measured after each week for one month. The serum separation rate was calculated from: (Sahin and Ozdemir, 2007).

$$\text{Serum separation (\%)} = \text{Serum weight} / \text{Ketchupweight} \times 100 \quad (6.4)$$



## **7. RESULTS AND DISCUSSION**

### **7.1. Electrical Conductivity and Surface Tension of Feed Solutions**

The polymers used for the electrospinning method and their electrical conductivity and surface tension are given in following table (Table 7.1). In this table, it was also given that whether these solutions produce nanofiber from the electrospinning.

The solutions given in Table 7.1 were fed to electrospinning. The operation conditions were in the ranges of 20-40 kV for the applied voltage, 0.1-6 ml/h for feed rate, and 8-15 cm for the distance between the tip and the collector plate. The Table 7.1 shows that fiber obtained only by feeding gelatin (7, 10 and 20%) and gelatin-CA (3:1) solutions.

The reason that any fiber did not obtain from pectin or CA solution can be the high surface tension of solution. It is generally considered that the high surface tension of solution inhibits the electrospinning process, thereby resulting in the instability of the jets and the generation of sprayed droplets.(Hohman et al., 2001) Therefore, gelatin used as co-polymer. By adding gelatin solution to CA solution, the surface tension of CA solution decreased enough for electrospinning process. (Table7.1)

The only polymer which used alone and produced nanofiber was gelatin. This could be due to fact that the acetic acid solution used as solvent hydrolyses gelatin, therefore the gelatin can become more electrospinnable.

As shown in Table 7.1 the electrical conductivity of gelatin solution 7%, 10% and 20 % is  $2.45 \pm 0.04$ ,  $2.98 \pm 0.14$  and  $4.77 \pm 0.04$  mS / cm respectively. It can be observed that electrical conductivity of gelatin solutions are increased by increasing gelatin concentration, which this result come along with previous study by Ratanavaraporn et al. (2010). In their study formic acid was used as solvent and the electrical conductivity of gelatin solution increased from 2.91 to 4.71 mS / cm by increasing the gelatin concentration from 7.5% to 20%.

Since the electrical conductivity and surface tension of the solution are appropriate for the production of nanofiber formation, probably lower concentration of gelatin

solution is the problem. By increasing the gelatin concentration from 7% to 20%, electrospinning process was improved.

Increase in the concentration of polymers containing ionic components within the solution caused an increase in conductance, while the opposite is the case for polymers containing ionic components on site (Andrady, 2008).

In contrast, with increasing the concentration of gelatin solution, the decrease in surface tension was observed. The surface tension of gelatin solution 7%, 10% and 20 % is  $35.91 \pm 0.03$ ,  $35.61 \pm 0.03$  and  $35.57 \pm 0.03$  mN/m respectively. This result is consistent with the literature. In a study by Lin and Chen (2006) the surface tension of gelatin solution decreased from 65 to 30 mN/m by increasing gelatin concentration from 0.2% to 1.8%. Therefore the gelatin solution with higher concentration has lower surface tension which improve the electrospinning process. However, not necessarily a lower surface tension of a solvent will always be more suitable for electrospinning. Basically, surface tension determines the upper and lower boundaries of the electrospinning window if all other variables are held constant (Fong et al., 1999; Zhang et al., 2005b; Pham et al., 2006).

In addition from Table 7.1, the gelatin solution 10% including CA 17% has the electrical conductivity of  $0.75 \pm 0.01$  mS / cm and surface tension of  $42.20 \pm 0.03$  mN/m. Therefore, for improving electrospinning of blend solution higher voltage is needed to overcome the high amount of surface tension

**Table 7.1:** Properties and electrospinnability of feed solutions.

Polymer	Co-polymer	Blend ratio (v/v)	Nanofiber production(*)	Electrical conductivity (mS/cm)	Surface tension (mN/m)
%2 Pectin	-	-	-	0.64 ± 0.00	67.58 ± 0.03
%3 Pectin	-	-	-	0.70 ± 0.00	64.63 ± 0.03
%7 Gelatin	-	-	+	2.45 ± 0.04	35.91 ± 0.03
%10 Gelatin	-	-	+	2.98 ± 0.14	35.61 ± 0.03
%2 Pectin	%10 Gelatin	(1:2)	-	2.75 ± 0.00	35.79 ± 0.03
%2 Pectin	%10 Gelatin	(1:5)	-	2.91 ± 0.04	35.58 ± 0.03
%3 Pectin	%10 Gelatin	(1:2)	-	2.68 ± 0.01	35.48 ± 0.03
%3 Pectin	%10 Gelatin	(1:5)	-	2.85 ± 0.00	34.00 ± 0.03
%0.2 Xanthan gum	-	-	-	1.25 ± 0.01	65.54 ± 0.03
%10 CA	-	-	-	0.12 ± 0.01	64.87 ± 0.03
%17 CA	-	-	-	0.10 ± 0.01	67.22 ± 0.03
%17 CA	%10 Gelatin	(1:3)	+	0.75 ± 0.01	42.20 ± 0.03
%20 Gelatin	-	-	+	4.77 ± 0.04	35.57 ± 0.03
%2 CMC	-	(1:5)	-	2.56 ± 0.04	40.25 ± 0.03
%3 CMC	-	(1:2)	-	2.58 ± 0.05	42.98 ± 0.03
%2 CA	Gelatin 20%	(1:3)	-	0.90 ± 0.05	39.65 ± 0.03
%3 CA	Gelatin 20%	(1:3)	-	0.85 ± 0.14	41.24 ± 0.03
%5 Inulin	-	-	-	0.074 ± 0.01	58.24 ± 0.03

\* (+) means that nanofiber can be obtained successfully from electrospinning whereas (-) means that no nanofiber can be produced.

## 7.2. Rheological Properties of Feed Solutions

K and n values of feed solutions are provided in the following table (Table 7.2).

**Table 7.2:** K and n values of feed solutions.

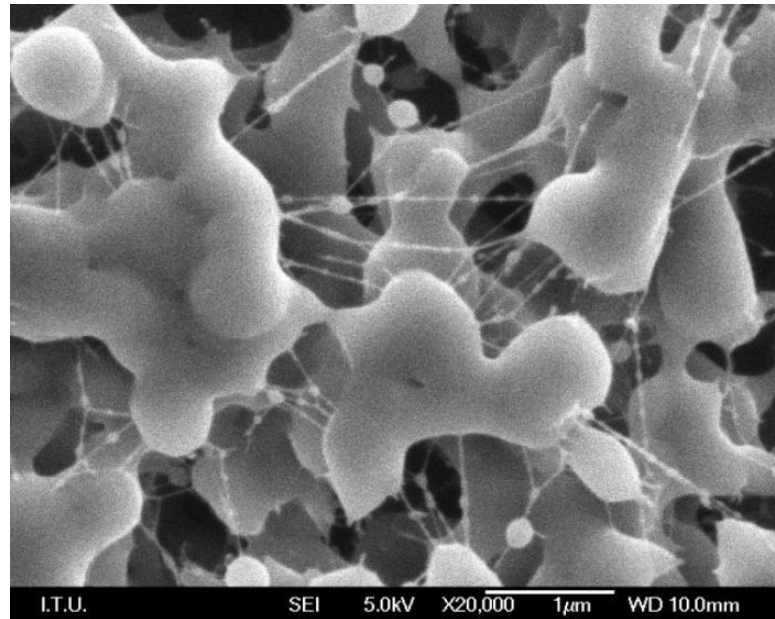
Solution	K (Pa.s <sup>n</sup> )	n (-)
Gelatin 7%	0.041 ± 0,00	0.80 ± 0,03
Gelatin 10%	0.75 ± 0.05	0.50 ± 0.01
Gelatin 20%	1,51 ± 0,05	0,46 ± 0,01
CA 17%	9.34 ± 0.01	0.92 ± 0.03
The 3:1 ratio of gelatin 10% and CA 17%	1.70 ± 0.05	0.48 ± 0.05

According to rheological properties of solutions they are all pseudoplastic ( $n < 1$ ). Because the n value of CA solution 17% is closer to 1 compare to other solutions, therefore it shows more Newtonian flow behavior. It is well known that the higher total solids cause higher consistency. However, no nanofiber obtained by CA solution. This is probably because of highly concentrated solutions usually hinder the flow through the capillary, thus negatively affecting the process.

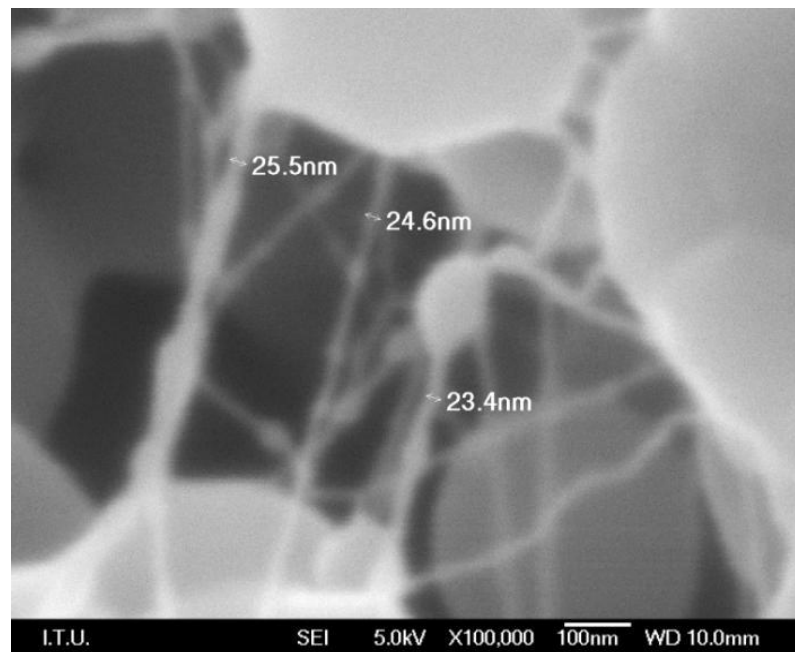
## 7.3. SEM Characterization of Nanofibers

SEM image of electrospun samples obtained from gelatin solution at 7% is shown in Figure 7.1 and 7.2, in two different magnifications. It was not possible, even by changing the parameters, to obtain nanofiber from gelatin solution at 7 % (Figure 7.1). This is because of low solution concentration. This result come along with study by Deitzel et al., (2001), Liu and Hsieh (2002), Ryu et al., (2003), McKee et al., (2004), Ki et al., (2005) and Haghi and Akbari (2007). They investigated that the electrospinning process, for fiber formation to occur, a minimum solution concentration is required. It has been found that at low solution concentration, a mixture of beads and fibers is obtained and as the solution concentration increases.



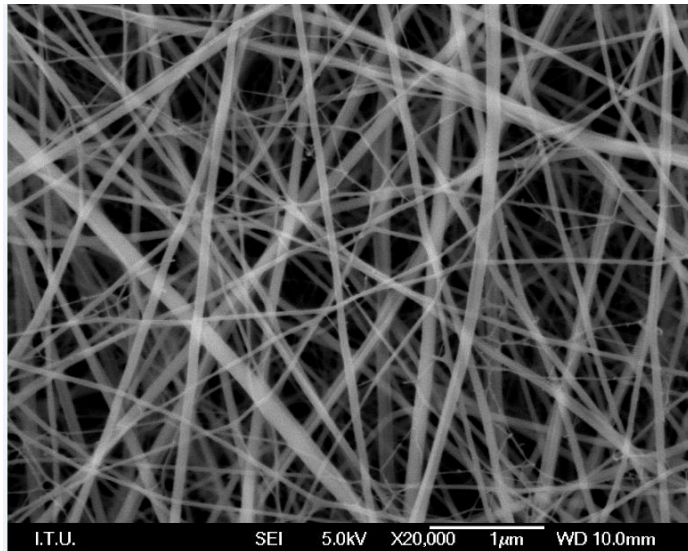


**Figure 7.1:**SEM image ( $\times 20000$ ) of nanofiber obtained from gelatin solution at 7% .

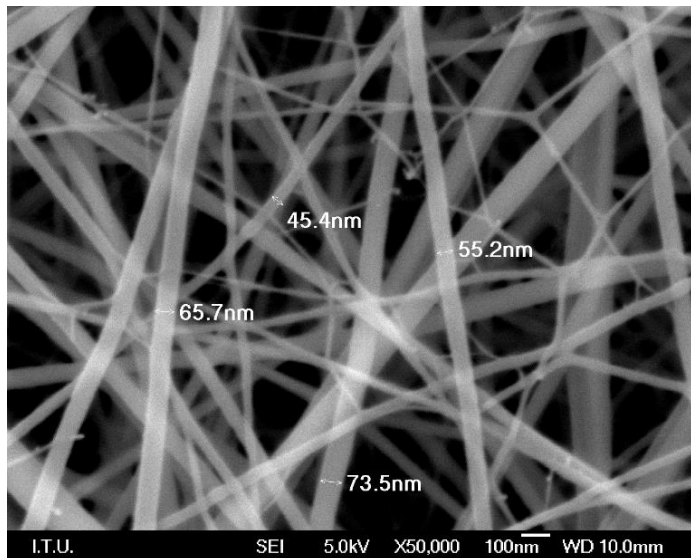


**Figure 7.2:**SEM image ( $\times 100000$ ) of nanofiber obtained from gelatin solution at 7%.

SEM images of nanofiber obtained from gelatin solution at 20% are shown in Figure 7.3 and 7.4, in two different magnifications. The shape of the beads changes from spherical to spindle-like and finally uniform fibers with increased diameters are formed because of the higher viscosity (Deitzel et al., 2001; Liu and Hsieh, 2002; Ryu et al., 2003; McKee et al., 2004; Ki et al., 2005; Hagi and Akbari, 2007).

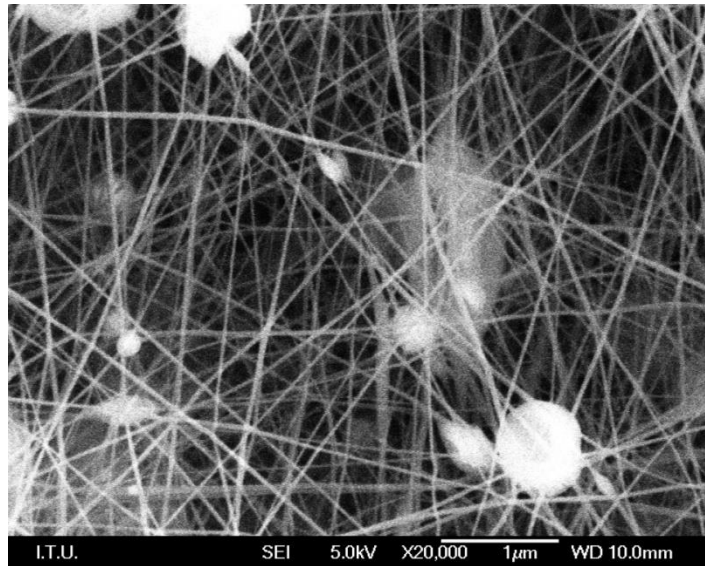


**Figure 7.3:**SEM image ( $\times 20000$ ) of nanofiber obtained from gelatin solution at 20%.

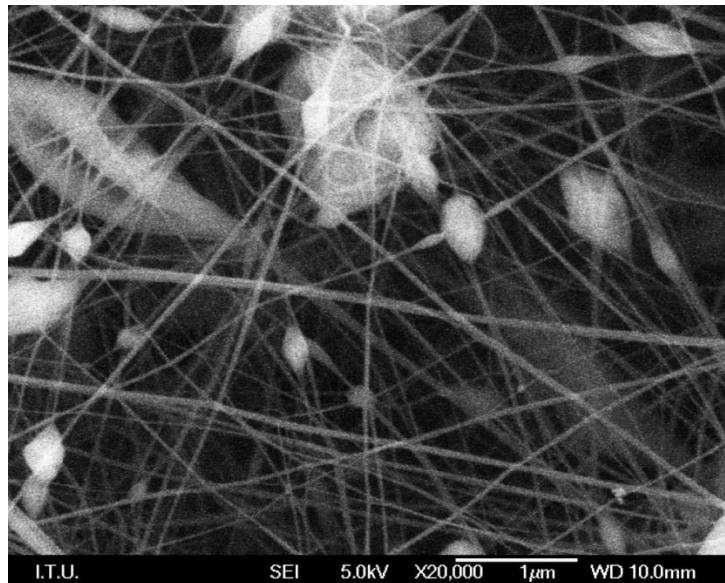


**Figure 7.4:**SEM image ( $\times 50000$ ) of nanofiber obtained from gelatin solution at 20%.

SEM images of nanofiber obtained from gelatin solution at 10% containing CA 17% (3:1) by three different electrospinning parameters are shown in Figure 7.5 , 7.6 and 7.7.

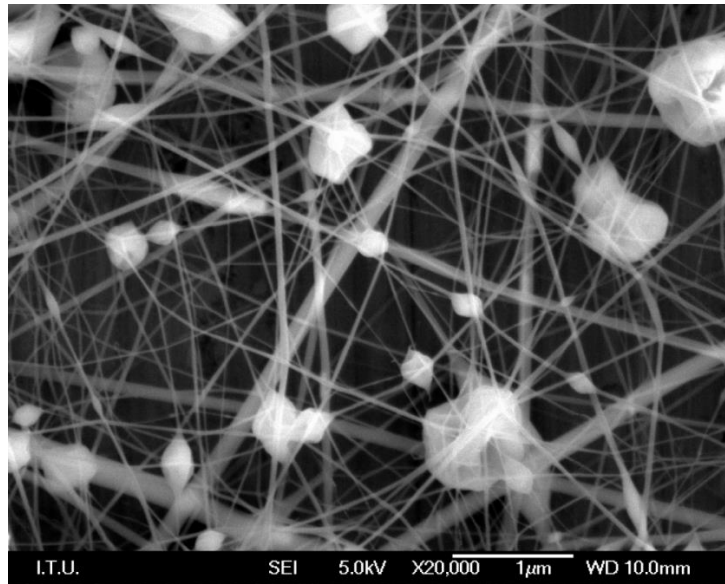


**Figure 7.5:** SEM image ( $\times 20000$ ) of nanofiber obtained from gelatin-CA solution (40 kV, 1ml/hr, 7cm)



**Figure 7.6:** SEM image ( $\times 20000$ ) of nanofiber obtained from gelatin-CA solution (40 kV, 1ml/hr, 10cm).

Different electrospinning parameters tested for the gelatin-CA solutions. According to the SEM images, gelatin-CA nanofiber obtained by following electrospinning parameters used in this study: Voltage: 40 kV, Distance: 7 cm, Feed solution rate: 1 ml/ hr.



**Figure 7.7:**SEM image ( $\times 20000$ ) of nanofiber obtained from gelatin-CA solution (25 kV, 1ml/hr, 10cm).

From these figures it can be seen by electrospinning of gelatin-CA a mixture of nanofiber and beads formed, that can be result of low electrical conductivity or high surface tension of blend solution.

#### 7.4. Zeta Potential and Diffusion Coefficient of dispersions with nanofibers

In the following table (Table 7.3) zeta potential and diffusion coefficient of samples are provided.

**Table 7.3:** Zeta potential and diffusion coefficient of dispersions with nanofibers.

Sample (all samples were dispersed at 0.1% (w/v) in ethanol)	Zeta potential (mV)	Diffusion coefficient ( $\mu\text{m}^2/\text{s}$ )
Electrospun samples from gelatin solution at 7%	5,47 $\pm$ 0,10	0,46 $\pm$ 0,08
Electrospun samples from gelatin solution at 10%	6,49 $\pm$ 0,02	0,59 $\pm$ 0,06
Electrospun samples from gelatin solution at 20%	16.06 $\pm$ 0.08	1.21 $\pm$ 0.04
Electrospun samples from gelatin solution(at 10%)- CA solution (at 17%) (3:1)	20.78 $\pm$ 0.04	1.81 $\pm$ 0.00
Gelatin (bulk)	-0,49 $\pm$ 0,04	0,02 $\pm$ 0,00

Table 7.3 shows that the diffusion coefficient and zeta potential of all gelatin electrospun nanofiber were higher than gelatin at bulk state. This result come along

with the definition of nanotechnology by National Nanotechnology Initiative (NNI), which is “At the nanoscale, the physical, chemical, and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter.”

The zeta potential is crucial in determining the stability of a suspension. If all the particles have a large negative or positive zeta potential then they will tend to repel each other, and there will be no tendency for the particles to come together, so the suspension will be stable. However, if the zeta potential is low there will be insufficient repulsion to prevent the particles coming together, so the tendency for flocculation is increased. For the samples containing nanofibers with only gelatin the highest zeta potential value of dispersion was the one obtained from gelatin solution at 20% (Table 7.3). Keeping all dispersions have the same concentration in mind, it is interesting to note that the zeta potential values increased with the concentration of the feed solution. This may be attributed the higher concentration of feed solution resulted in higher fiber diameter, which gave higher zeta potential probably due to higher surface area of samples in the dispersion. This explanation may be extended to the zeta potential of sample with nanofiber containing gelatin-CA. As seen from the SEM images (Fig 7.5, 7.6 and 7.7), the nanofibers from the blend of gelatin and CA solutions resulted in morphologies with beads, which increased the surface area of the samples. It may also be the reason for the higher zeta potential value of dispersion containing those nanofibers. It should also be noted that the dispersion with nanofibers containing gelatin-CA had less tendency to sediment compared to other dispersions.

The diffusion coefficient (also called as diffusivity) is a measure the ability of a molecule to diffuse into another molecule, higher the diffusion coefficient, higher the mobility. The diffusion coefficient of gelatin nanofibers in ethanol increased with the concentration of feed solution (Table 7.3). Similar to the zeta potential values, diffusion coefficient value of dispersion with nanofibers containing gelatin-CA was the highest. This may be explained with the increasing surface area of nanofibers: more surface area may increase the interaction with the solvent, probably led to increased diffusion coefficient.

It appears that the electrospinning conditions that affect the morphology and surface characteristics of nanofibers may influence the other properties of the nanofibers such as zeta potential and diffusion coefficient. This point may be taken into account for designing nanofibers as they are needed.

## 7.5. Rheological Properties of Tomato Ketchup Samples

Some rheological parameters of tomato ketchup, by the Power-Law and the Herschel-bulkley models, were investigated and the values are shown in Table 7.4.

**Table 7.4:** Rheological parameters of commercial tomato Ketchup.

Sample	Consistency index K'(Pa.s <sup>n</sup> )	Flow behavior index n'	Yield Stress $\tau_0$ (Pa)	Consistency index K(Pa.s <sup>n</sup> )	Flow behavior index n
Commercial tomato ketchup	7.26±0.05	0.49±0.01	34.40±0.01	10.13±0.02	0.50±0.00

The flow behavior indices values (n and n') for the tomato ketchup is given in Table 7.4. Since the n and n' value is smaller than 1 (Table 7.4) commercial ketchup is pseudoplastic with yield stress. These results come along with results from Bottiglieri et al. (1991). They investigated that ketchups are time-independent, non-Newtonian fluids that show a small thixotropy.

### 7.5.1. Effect of nanofiber addition on rheology of tomato ketchup

The rheological properties of tomato ketchup samples by the Power-law and the Herschel-bulkley models are given in Tables 7.5, 7.6, 7.7 and 7.8. The consistency index values of tomato ketchup including nanofibers at two different temperatures (4 and 25°C) are shown in Tables 7.5, 7.6, 7.7 and 7.8. It is obvious from the tables the addition of electrospun nanofibers led to an increase in the consistency indices (K and K') of the tomato ketchups. It is well known that the higher the total solids the better will be the quality of the end product. Therefore as the percentage of the nanofiber increased, the consistency indices (K and K') increased.

**Table 7.5:** Rheological parameters of ketchup samples at 7<sup>th</sup> day. ( by Power-law and Herschel-bulkley models)

Samples	Storage Temperature	Power-law model		Herschel-bulkley model		n'
		K (Pa.s <sup>n</sup> )	n	$\tau_o$ (Pa)	K' (Pa.s <sup>n</sup> )	
Ketchup (without nanofiber)	4°	<b>10.42±0.03</b>	<b>0.26±0.01</b>	<b>5.29±0.07</b>	<b>8.59± 0.03</b>	<b>0.27± 0.01</b>
	25°	6.48±0.01	0.44±0.01	5.11±0.02	5.34± 0.01	0.27± 0.00
Ketchup (with 0.25 % gelatin nanofiber)	4°	<b>13.65±0.08</b>	<b>0.18±0.00</b>	<b>20.02±0.05</b>	<b>11.18±0.02</b>	<b>0.21± 0.01</b>
	25°	7.72 ±0.00	0.41±0.01	19.83±0.00	7.69± 0.01	0.18± 0.01
Ketchup (with 0.5 % gelatin nanofiber)	4°	<b>25.10±0.01</b>	<b>0.17±0.01</b>	<b>24.09±0.02</b>	<b>20.82± 0.04</b>	<b>0.19± 0.00</b>
	25°	10.78±0.01	0.36±0.00	22.60±0.02	8.31± 0.01	0.21± 0.01
Ketchup (with 0.5 % gelatin-CA nanofiber)	4°	<b>32.78±0.02</b>	<b>0.11±0.02</b>	<b>35.01 ±0.04</b>	<b>28.94± 0.08</b>	<b>0.18± 0.00</b>
	25°	28.66±0.02	0.42±0.01	25.38±0.02	19.89± 0.01	0.19± 0.00

Koocheki et al. (2009) in their previous study investigated that the consistency indices increased with the concentration of hydrocolloids showing that addition of hydrocolloids stabilizes the consistency of the ketchup. The increase in the consistency indices were highest with the addition of gelatin-CA nanofiber and the least without any nanofiber (Tables 7.5, 7.6, 7.7 and 7.8).

**Table 7.6:** Rheological parameters of ketchup samples at 14<sup>th</sup> day. ( by Power-law and Herschel-bulkley models)

Samples	Storage Temperature	Power-law model		Herschel-bulkley model		n'
		K (Pa.S <sup>n</sup> )	N	$\tau_0$ (Pa)	K' (Pa.S <sup>n</sup> )	
Ketchup (Without nanofiber)	4°	15.35±0.03	0.52±0.02	6.17±0.02	13.80± 0.02	0.49± 0.00
	25°	8.93±0.02	0.40±0.00	6.09±0.01	5.93± 0.01	0.50± 0.00
Ketchup (with 0.25 % gelatin nanofiber)	4°	17.90±0.03	0.49±0.00	24.95±0.02	17.01±0.02	0.36± 0.02
	25°	14.44±0.01	0.38±0.00	20.21±0.15	12.79± 0.02	0.41± 0.03
Ketchup (with 0.5 % gelatin nanofiber)	4°	41.69±0.01	0.35±0.00	25.13±0.03	35.04± 0.03	0.33± 0.04
	25°	16.05±0.02	0.22±0.03	21.13±0.00	13.65± 0.10	0.32± 0.00

It is clear from Tables 7.5, 7.6, 7.7 and 7.8 that, K and K' decreased as storage temperature increase. At a given temperature, K and K' increased with increase in nanofiber addition. These results can be confirmed with the data obtained by Gujral et al., (2002) who reported that storage temperature affects the consistency index of tomato ketchup containing hydrocolloids.



**Table 7.7:**Rheological parameters of ketchup samples at 21<sup>th</sup> day. ( by Power-law and Herschel-bulkley models)

Samples	Storage Temperature	Power-law model		Herschel-bulkley model		
		K (Pa.S <sup>n</sup> )	N	$\tau_o$ (Pa)	K' (Pa.S <sup>n</sup> )	n'
Ketchup (Without nanofiber)	4°	12.35±0.02	0.45±0.03	4.91±0.02	11.00± 0.00	0.42± 0.00
	25°	11.60±0.00	0.49±0.00	4.88±0.04	10.35± 0.03	0.46± 0.00
Ketchup (with 0.25 % gelatin nanofiber)	4°	14.90±0.01	0.42±0.00	23.52±0.01	13.89±0.03	0.40±0.01
	25°	13.95±0.01	0.42±0.00	20.58±0.02	10.98± 0.02	0.39±0.02
Ketchup (with 0.5 % gelatin nanofiber)	4°	15.92±0.00	0.37±0.01	29.99±0.02	14.86± 0.01	0.40± 0.00
	25°	14.34±0.01	0.19±0.01	24.36±0.05	11.22± 0.00	0.26±0.01

The values for the flow behaviour index were always lower than one, which indicates the pseudoplastic nature of tomato ketchup. This is in accordance with previous works (Varela et al., 2003; Muller, 1973; Upasana Rani and Bains, 1987).

The ketchup does not flow until reaching a certain levels of stress (called yield stress). Yield stress ( $\tau_0$ ) value was higher for samples contained nanofibers and lower for the ketchup sample without any nanofiber. Farahnaky et al. (2008) used tomato pulp powder as a thickening agent in the formulation of tomato ketchups at different levels (1, 2, 5, 7 and 10 % w/w). They also observed, an increase in the yield stress as they increased the level of pulp powder, and they suggested the ability of the pulp powder to absorb water, and the increase in the total solids of the samples as a result of the addition of the pulp powder can be consider as the reason of the increase in yield stress.

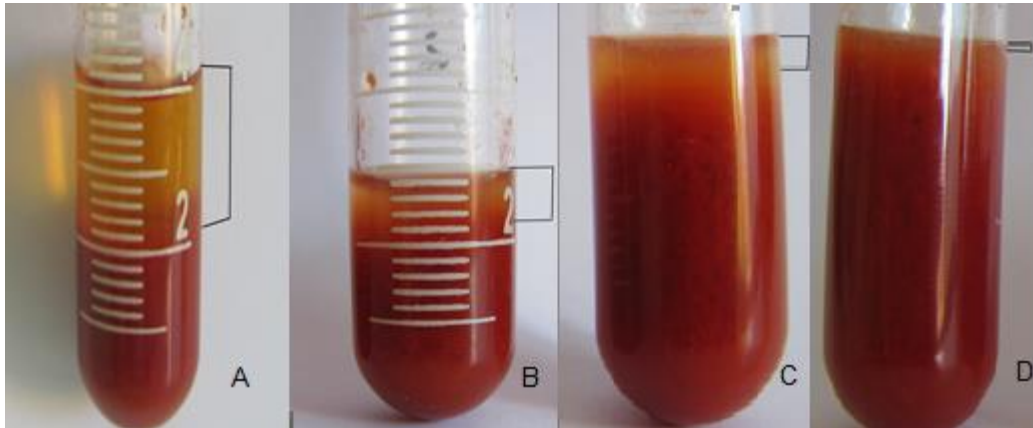
Moreover, from Tables 7.5, 7.6, 7.7 and 7.8 it could be observed that yield stress point for all ketchup samples decreased when the storage temperature increased. This result is in accordance with the study by Koocheki (2009).

**Table 7.8:** Rheological parameters of ketchup samples at 28<sup>th</sup> day. ( by Power-law and Herschel-bulkley models)

Samples	Storage Temperature	Power-law model		Herschel-bulkley model		
		K (Pa.S <sup>n</sup> )	n	$\tau_o$ (Pa)	K' (Pa.S <sup>n</sup> )	n'
Ketchup (Without nanofiber)	4°	8.85±0.00	0.50±0.00	6.03±0.05	5.97± 0.04	0.48± 0.01
	25°	6.73±0.01	0.50±0.00	5.99±0.03	5.41± 0.01	0.50± 0.00
Ketchup (with 0.25 % gelatin nanofiber)	4°	13.30±0.00	0.24±0.01	23.90±0.02	13.13± 0.01	0.29± 0.01
	25°	9.45±0.00	0.38±0.03	22.45±0.05	7.14± 0.04	0.29± 0.01
Ketchup (with 0.5 % gelatin nanofiber)	4°	18.93±0.01	0.12±0.00	34.94±0.11	17.54± 0.00	0.12± 0.03
	25°	12.11±0.02	0.15±0.02	25.10±0.01	9.51± 0.01	0.13± 0.01

## 7.6. Serum Separation Measurement of Ketchup Samples

Water separation (syneresis) in samples was determined. In Figure 7.8 results for some nanofiber added samples are given. As shown in the figure increasing fiber amount reduced the water separation in the tubes.



**Figure 7.8:** Ketchup samples after centrifugation force 2000g after 7<sup>th</sup> day storage at 4 °C. (A: Ketchup sample without nanofiber, B: Ketchup sample with 0.25% gelatin nanofiber, C: ketchup sample with 0.5% gelatin nanofiber, D: Ketchup sample with 0.5% gelatin-CA nanofiber).

From Figure 7.8, the maximum syneresis after centrifuge force 2000g belongs to ketchup sample without any nanofiber (A), and the least one belongs to ketchup including 0.5% gelatin-CA nanofiber (D).

In Figure 7.9 serum separation versus time, for nanofiber added samples which were kept in two different temperatures, are shown. This test is done in duplicate size, and the average percentage is shown in Figure 7.9.

The centrifuge tests are done after each week for one month. As shown in the Figures 7.8 and 7.9, fiber addition dramatically improved the stability of the ketchup samples. However, the storage time seems has no effect in serum separation. In all cases the serum separation percentage at 4°C is less than 25°C. which this result come along with previous study by Gujral et al. (2002). They investigated serum loss decreased with the addition of all the hydrocolloids and increased with the increase in storage temperature. They found that the more serum separation reason at higher temperature could be attributed to the presence of a small amount of protein as an integral part of its molecule and the gum undergoes auto hydrolysis at higher

temperatures for prolonged periods resulting in the precipitation of the protein rich fraction. As shown in the Figure (7.9) and Tables (7.7-11) samples without any nanofiber addition had the highest rate of separation, and the least one is the gelatin-CA nanofiber added ketchup samples. The gelatin-CA nanofiber has the highest amount of diffusion coefficient and zeta potential comparing to gelatin nanofibers. It can be concluded that maybe because of high diffusion coefficient of gelatin-CA nanofibers, they have more interaction with other molecules that decrease syneresis. In addition, the high zeta potential value of nanofibers containing gelatin-CA may help ketchup samples more stable.

In addition from Figure 7.9 it can be seen that the storage time didn't affect serum separation, it can be because of the high water holding capacity of nanofiber. This result is in contrast with study by Gujral et al. (2002). They investigated that tomato ketchup containing hydrocolloids showed an increase in serum loss during storage. This could be attributed to the hydrolysis of the hydrocolloids, as a result they lost their water holding capacity. However, in present study, the serum separation didn't change during storage time. This indicates that nanofiber have excellent water holding capacity and are excellent in preventing the occurrence of syneresis in tomato ketchup during storage.

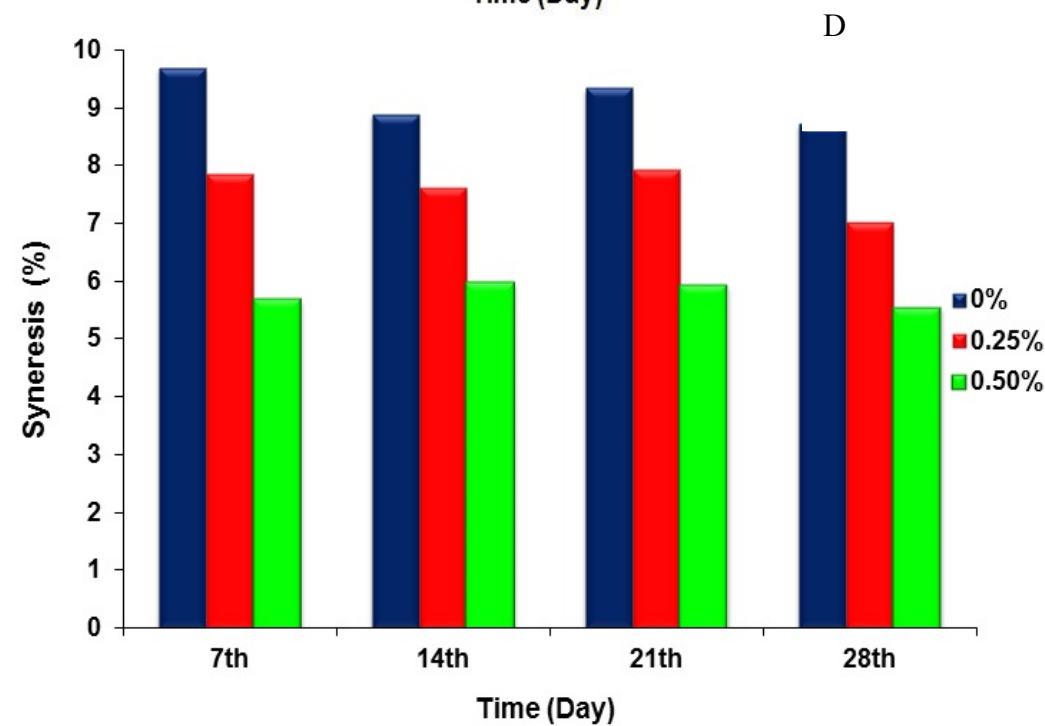
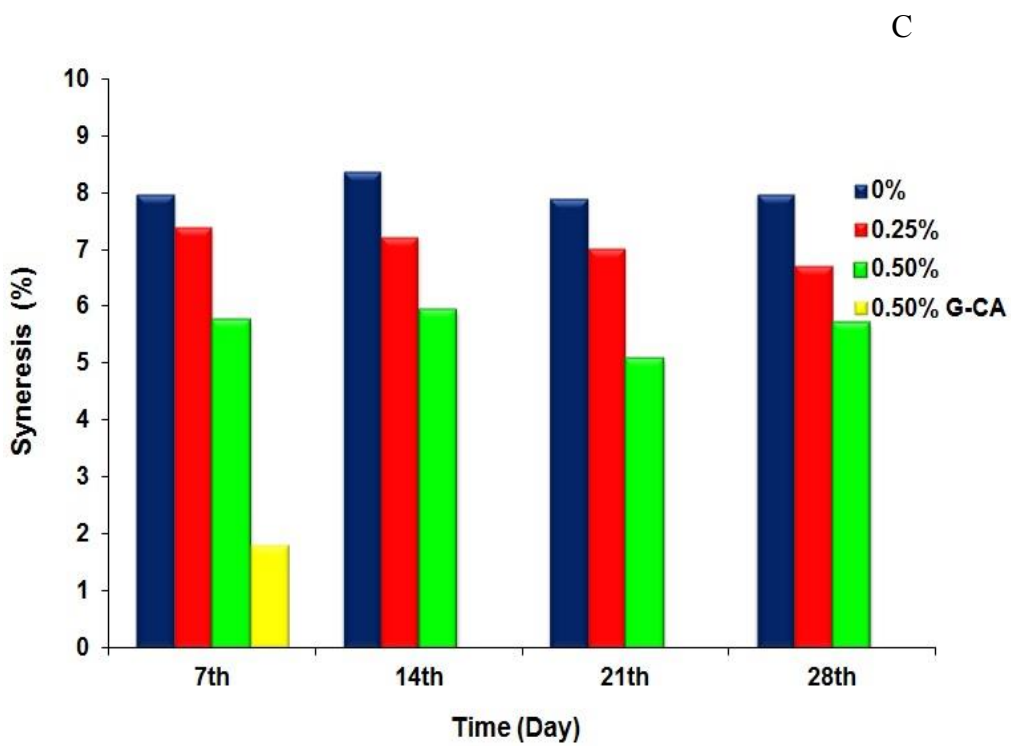
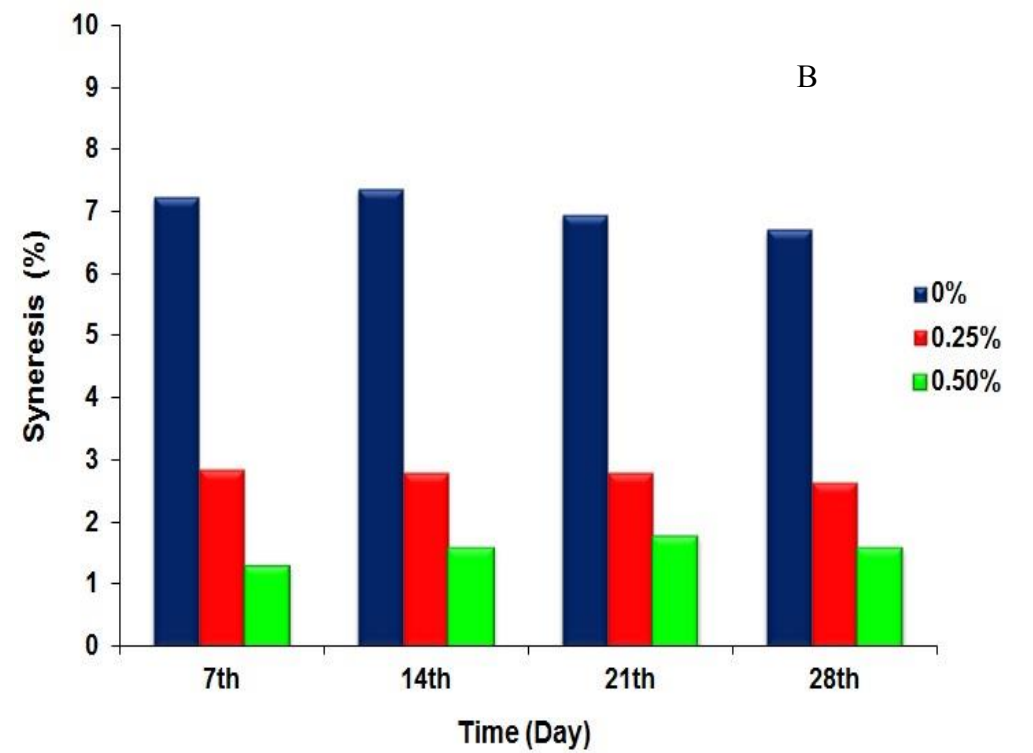
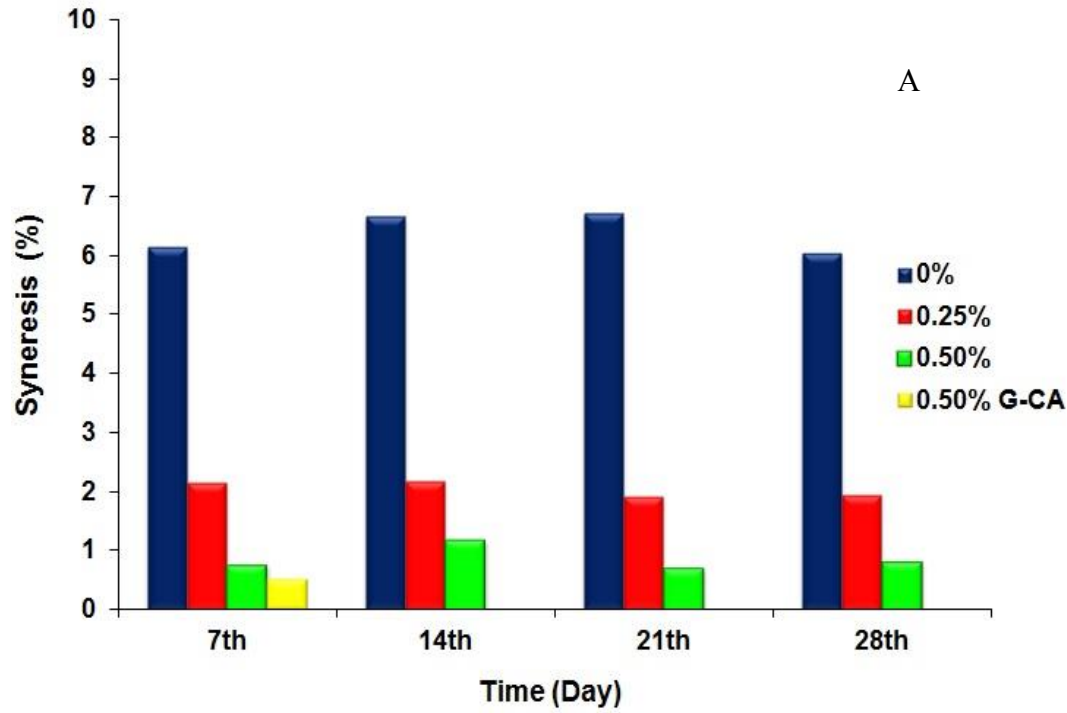


Figure 7.9: Syneresis-time bar-graph for ketchup samples. (A: samples stored at 4°C, centrifuge force 2200g; B: samples stored at 25°C, 2200g; C: samples stored at 4°C, 5000g; D: samples stored at 25°C, 5000g).

## 8. CONCLUSIONS

The present study showed that gelatin and gelatin-CA electrospun nanofiber can be used to improve texture and decrease serum separation of tomato ketchup.

According to SEM images, electrospinning of gelatin solution at 7% produced a mixture of beads and fibers, the reason was low concentration of the feed solution. But by increasing the gelatin concentration from 7 to 20% the morphology turned to uniform fibers. In addition, SEM images of nanofiber obtained from gelatin-CA solution showed the highest concentration of nanofiber obtained by these electrospinning parameters; 40 kV voltage, 7 cm distance between the tip to collector plate and 1ml/hr feed solution rate.

The zeta potential and diffusion coefficient results showed that there is a meaningful difference between these values of gelatin in bulk size and gelatin at nanoscale. The properties of nanofibers are affected by nanofiber composition. The dispersions with gelatin-CA nanofibers has the greatest zeta potential and diffusion coefficient values.

Electrospun gelatin samples higher diffusivities than gelatin powder meaning electrospinning may increase the ability of samples to diffuse comparing to gelatin powder. Diffusion coefficient measurements of nanofiber dispersion in ethanol showed the diffusion coefficient increase with gelatin concentration in the dispersion, and gelatin-CA nanofiber dispersion has the highest diffusion coefficient. Therefore, these dispersions with gelatin-CA nanofiber may have more stable structure containing particles with higher diffusion ability, which may cause more interactions with water molecules and eventually decrease serum separation in ketchup.

The rheological data of the samples with and without the nanofiber showed that the nanofiber could be used instead of hydrocolloids or thickeners in the formulation of tomato ketchup. Moreover, these results indicated that ketchup supplemented with studied hydrocolloids (gelatin and gelatin-CA) in form of electrospun nanofiber, behave as non-Newtonian and pseudoplastic behavior with yield stress at 4 and 25° C storage temperatures. Furthermore, increasing the nanofiber concentration increased

the consistency indices compared to the control sample. The effect of gelatin-CA electrospun nanofiber on consistency was greater than gelatin electrospun nanofiber. The consistency indices ( $K$  and  $K'$ ) increased with the concentration of all nanofibers showing that addition of these nanofibers, even in small amount, stabilizes the consistency of the ketchup. Likewise, the addition of nanofiber increased yield stress as compared to sample without any nanofiber. In brief, all rheological parameters ( $K$ ,  $K'$  and  $\tau_0$ ) increased with the addition of nanofiber. Additionally, it is found the storage temperature affect both consistency indices and yield stress. These values decreased with increasing the storage temperature, therefore the ketchup samples stored at 4°C had less serum separation compared to ketchup samples stored at 25°C .

Moreover this result verified with the stability measurements data. Ketchup containing 0.5% gelatin-CA electrospun nanofiber stored at 4°C showed the lowest phase separation. Sahin and Ozdemir (2007) observed that the serum separation of the ketchups containing 1% of hydrocolloids was 7.32% at the end of the 900 hours of storage at ambient temperature. However, in our study, the serum separation of ketchup after one week storage at ambient temperature was 1.31% only by adding 0.5% of gelatin-CA nanofiber. Therefore the results from our study indicate that nanofiber composition and concentration even in very small amount had an effect on ketchup syneresis.

The addition of nanofiber improved the stability of the ketchup samples. It is probably because of water holding property of nanofiber in tomato ketchup. In other possible explanation may be the swelling of nanofibers in ketchup. This swelling or water holding capacity of nanofibers may cause to inhibit the syneresis in ketchups. These should be investigated by future research.

As future work, the effects of other hydrocolloid may be studied in terms of nanofiber composition and function to obtain the improved product quality. For instance different hydrocolloid may be used in emulsions, suspensions and foams in order to obtain improved stability, rheological and textural properties. Moreover, more rheological model, such as Casson and Bingham can be examined, in order to find which model is best fitted for tomato ketchup including nanofibers. In addition, for more physical characterization of nanofibers, transmission electron microscopy (TEM) and atomic force microscopy (AFM), and also for chemical characterization of nanofibers Fourier transform infra red (FTIR), nuclear magnetic resonance



(NMR), circular dichroism (CD), differential scanning calorimetry (DSC), X-ray diffraction and X-rayscattering can be used.

As a conclusion, the future of nanotechnology applications in foods appears to need further research including toxicity studies of nanomaterials. The start point of this study was to obtain same or better results with the addition of nanofibers which are very little amount compared to materials that are currently used in food industry for same functions. The outcomes showed that electrospun nanofibers have the potential for the start point of this study which is also the start point of nanotechnology applications. Therefore, the outcomes of the study seem very promising for the food industry. Indeed, if nanofibers with different functions which can be tailored by processing parameters during electrospinning will be added to foods to achieve better jobs than traditional additives or components in the food with lower amount, then it may be considered as beneficial in food industry's point of view. Accordingly, then, more research is need to be done for obtaining nanomaterials, characterization methods and applications for various objectives with different functions. In the future, the nanotechnology application in foods and food packaging will probably increase, which we can see the products in our dialy life.

However, there is one point should be taking into account, which is the risk evaluation of engineered nanomaterials. There is an apparent gap between the nanotechnology applications and concerns of consumers and manufacturers. In addition, the legislation about the utilization of engineered nanoparticles or nanotechniques are needed to be set to regulate nanotechnology applications in foods. In that case, nanotechnolgy applications will accelerate as predicted for food industry in the future.



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**APPENDICES:**

**APPENDIX A:** Diffusion coefficient of dispersions with nanofibers measurements.

**APPENDIX B:** Zeta potential of dispersions with nanofibers measurements.

**APPENDIX C:** Rheological measurements of ketchup samples.

**APPENDIX D:** Serum separation (%) of nanofiber added ketchup samples.

**APPENDIX E:** Flow curves of ketchup samples.

**APPENDIX F:** Zeta potential curves of nanofibers.

## APPENDIX A

**Table A.1:** Diffusion coefficient of dispersions with nanofibers measurements

Sample [all samples were dispersed at 0.1% (w/v) in ethanol]	Diffusion coefficient ( $\mu\text{m}^2/\text{s}$ )
Electrospun samples from gelatin solution at 7%	0.40, 0.52
Electrospun samples from gelatin solution at 10%	0.55, 0.64
Electrospun samples from gelatin solution at 20%	1.18, 1.25
Electrospun samples from gelatin solution(at 10%)- CA solution (at 17%) (3:1) nanofiber	1.81, 1.82
Gelatin (bulk)	0.02, 0.03



## APPENDIX B

**Table B.1: Zeta potential of dispersions with nanofibers measurements**

Sample [all samples were dispersed at 0.1% (w/v) in ethanol]	Zeta potential (mV)
Electrospun samples from gelatin solution at 7%	5.40, 5.55
Electrospun samples from gelatin solution at 10%	6.48, 6.51
Electrospun samples from gelatin solution at 20%	16.00, 16.12
Electrospun samples from gelatin solution(at 10%)- CA solution (at 17%) (3:1) nanofiber	20.75, 20.82
Gelatin (bulk)	- 0.46, - 0.52

## APPENDIX C

**Table C.1:** Rheological measurements of ketchup samples by Power-law model (at 4 °C, 7<sup>th</sup> day).

Sample	K	n
Ketchup (including 0 % gelatin nanofiber)	10.39, 10.41, 10.46	0.25, 0.27, 0.27
Ketchup (including 0.25 % gelatin nanofiber)	13.74, 13.65, 13.58	0.18, 0.18, 0.18
Ketchup (including 0.5 % gelatin nanofiber)	25.11, 25.09, 25.11	0.17, 0.19, 0.17
Ketchup (including 0.5 % gelatin-CA nanofiber)	32.78, 32.81, 32.77	0.11, 0.09, 0.13

**Table C.2:** Rheological measurements of ketchup samples by Power-law model (at 4 °C, 14<sup>th</sup> day).

Sample	K	n
Ketchup (including 0 % gelatin nanofiber)	8.94, 8.95, 8.91	0.54, 0.49, 0.53
Ketchup (including 0.25 % gelatin nanofiber)	14.45, 14.45, 14.43	0.49, 0.49, 0.49
Ketchup (including 0.5 % gelatin nanofiber)	16.06, 16.08, 16.03	0.35, 0.36, 0.35

**Table C.3:** Rheological measurements of ketchup samples by Power-law model (at 4 °C, 21<sup>th</sup> day).

Sample	K	n
Ketchup (including 0 % gelatin nanofiber)	12.37, 12.33, 12.35	0.44, 0.49, 0.43
Ketchup (including 0.25 % gelatin nanofiber)	13.95, 13.97, 13.95	0.43, 0.42, 0.42
Ketchup (including 0.5 % gelatin nanofiber)	14.33, 14.33, 14.36	0.37, 0.39, 0.37

**Table C.4:** Rheological measurements of ketchup samples by Power-law model(at 4 °C, 28<sup>th</sup> day).

Sample	K	n
Ketchup (including 0 % gelatin nanofiber)	8.85, 8.86, 8.86	0.51, 0.51, 0.50
Ketchup (including 0.25 % gelatin nanofiber)	9.45, 9.45, 9.45	0.25, 0.23, 0.24
Ketchup (including 0.5 % gelatin nanofiber)	12.11, 12.09, 12.13	0.12, 0.12, 0.13

**Table C.5:**Rheological measurements of ketchup samples by Power-law model(at 25 °C, 7<sup>th</sup> day).

Sample	K	n
Ketchup (including 0 % gelatin nanofiber)	6.47, 6.49, 6.50	0.43, 0.44, 0.45
Ketchup (including 0.25 % gelatin nanofiber)	7.73, 7.72, 7.72	0.42, 0.41, 0.40
Ketchup (including 0.5 % gelatin nanofiber)	10.79, 10.79, 10.76	0.36, 0.37, 0.37
Ketchup (including 0.5 % gelatin-CA nanofiber)	28.65, 28.69, 28.64	0.42, 0.42, 0.44

**Table C.6:**Rheological measurements of ketchup samples by Power-law model (at 25 °C, 14<sup>th</sup> day).

Sample	K	n
Ketchup (including 0 % gelatin nanofiber)	15.34, 15.39, 15.32	0.40, 0.40, 0.40
Ketchup (including 0.25 % gelatin nanofiber)	17.90, 17.91, 17.90	0.38, 0.39, 0.39
Ketchup (including 0.5 % gelatin nanofiber)	41.69, 41.69, 41.71	0.25, 0.19, 0.23

**Table C.7:** Rheological measurements of ketchup samples by Power-law model(at 25 °C, 21<sup>th</sup> day).

Sample	K	n
Ketchup (including 0 % gelatin nanofiber)	11.60, 11.61, 11.60	0.50, 0.50, 0.49
Ketchup (including 0.25 % gelatin nanofiber)	14.90, 14.90, 14.92	0.42, 0.42, 0.42
Ketchup (including 0.5 % gelatin nanofiber)	15.92, 15.93, 15.93	0.19, 0.18, 0.20

**Table C.8:** Rheological measurements of ketchup samples by Power-law model(at 25 °C, 28<sup>th</sup> day).

Sample	K	n
Ketchup (including 0 % gelatin nanofiber)	6.73, 6.73, 6.75	0.50, 0.51, 0.50
Ketchup (including 0.25 % gelatin nanofiber)	13.30, 13.31, 13.31	0.39, 0.35, 0.41
Ketchup (including 0.5 % gelatin nanofiber)	18.94, 18.92, 18.94	0.13, 0.18, 0.14

**Table C.9:** Rheological measurements of ketchup samples by Herschel-bulkley model (at 4 °C, 7<sup>th</sup> day).

Samples	$\tau_0$ (Pa)	$K'$ (Pa.S <sup>n</sup> )	$n'$
Ketchup (Without nanofiber)	5.21, 5.32, 5.34	8.56, 8.61, 8.62	0.26, 0.28, 0.29
Ketchup (including 0.25 % gelatin nanofiber)	20.02, 20.08, 19.98	11.20, 11.16, 11.19	0.20, 0.21, 0.22
Ketchup (including 0.5 % gelatin nanofiber)	25.00, 24.97, 25.01	20.79, 20.80, 20.88	0.20, 0.19, 0.20
Ketchup (including 0.5 % gelatin- CA nanofiber)	35.05, 35.02, 34.96	28.84, 29.00, 28.98	0.18, 0.19, 0.18

**Table C.10:** Rheological measurements of ketchup samples by Herschel-bulkley model (at 4 °C, 14<sup>th</sup> day).

Samples	$\tau_o$ (Pa)	$K'$ (Pa.S <sup>n</sup> )	$n'$
Ketchup (Without nanofiber)	6.18, 6.20, 6.15	13.80, 13.79, 13.83	0.50, 0.49, 0.50
Ketchup (including 0.25 % gelatin nanofiber)	24.98, 24.94, 24.93	17.00, 17.00, 17.04	0.38, 0.34, 0.38
Ketchup (including 0.5 % gelatinnanofiber)	25.11, 25.13, 25.17	35.01, 35.06, 35.07	0.30, 0.32, 0.38

**Table C.11:** Rheological measurements of ketchup samples by Herschel-bulkley model (at 4 °C, 21<sup>th</sup> day).

Samples	$\tau_o$ (Pa)	$K'$ (Pa.S <sup>n</sup> )	$n'$
Ketchup (Without nanofiber)	4.92, 4.89, 4.94	11.01, 11.00, 11.00	0.43, 0.42, 0.43
Ketchup (including 0.25 % gelatin nanofiber)	23.50, 23.53, 23.53	13.93, 13.89, 13.87	0.39, 0.41, 0.41
Ketchup (including 0.5 % gelatinnanofiber)	30.02, 29.98, 29.99	14.87, 14.85, 14.87	0.40, 0.40, 0.40

**Table C.12:** Rheological measurements of ketchup samples by Herschel-bulkley model (at 4 °C, 28<sup>th</sup> day).

Samples	$\tau_o$ (Pa)	$K'$ (Pa.S <sup>n</sup> )	$n'$
Ketchup (Without nanofiber)	5.98, 6.02, 6.09	5.98, 6.01, 5.93	0.48, 0.48, 0.50
Ketchup (including 0.25 % gelatin nanofiber)	23.93, 23.89, 23.90	13.12, 13.13, 13.14	0.28, 0.31, 0.28
Ketchup (including 0.5 % gelatinnanofiber)	34.81, 35.00, 35.02	17.54, 17.55, 17.55	0.10, 0.12, 0.16

**Table C.13:** Rheological measurements of ketchup samples by Herschel-bulkley model (at 25 °C, 7<sup>th</sup> day).

Samples	$\tau_o$ (Pa)	$K'$ (Pa.S <sup>n</sup> )	$n'$
Ketchup (Without nanofiber)	5.11, 5.09, 5.13	5.34, 5.34, 5.36	0.28, 0.28, 0.27
Ketchup (including 0.25 % gelatin nanofiber)	19.83, 19.84, 19.84	7.70, 7.68, 7.70	0.20, 0.18, 0.18
Ketchup (including 0.5 % gelatin nanofiber)	22.58, 22.63, 22.59	8.31, 8.30, 8.33	0.21, 0.23, 0.21
Ketchup (including 0.5 % gelatin- CA nanofiber)	25.36, 25.40, 25.40	19.88, 19.90, 19.90	0.19, 0.19, 0.20

**Table C.14:** Rheological measurements of ketchup samples by Herschel-bulkley model (at 25 °C, 14<sup>th</sup> day).

Samples	$\tau_o$ (Pa)	$K'$ (Pa.S <sup>n</sup> )	$n'$
Ketchup (Without nanofiber)	6.08, 6.09, 6.11	5.94, 5.94, 5.91	0.50, 0.50, 0.50
Ketchup (including 0.25 % gelatin nanofiber)	20.04, 20.32, 20.29	12.80, 12.76, 12.81	0.42, 0.38, 0.44
Ketchup (including 0.5 % gelatin nanofiber)	21.13, 21.14, 21.13	13.73, 13.70, 13.54	0.33, 0.32, 0.32

**Table C.15:** Rheological measurements of ketchup samples by Herschel-bulkley model (at 25 °C, 21<sup>th</sup> day).

Samples	$\tau_o$ (Pa)	$K'$ (Pa.S <sup>n</sup> )	$n'$
Ketchup (Without nanofiber)	4.83, 4.91, 4.90	10.34, 10.40, 10.33	0.45, 0.46, 0.46
Ketchup (including 0.25 % gelatin nanofiber)	20.56, 20.58, 20.61	11.00, 10.95, 10.99	0.42, 0.39, 0.38
Ketchup (including 0.5 % gelatin nanofiber)	24.31, 24.35, 24.42	11.23, 11.22, 11.22	0.28, 0.26, 0.26

**Table C.16:** Rheological measurements of ketchup samples by Herschel-bulkley model (at 25 °C, 28<sup>th</sup> day).

Samples	$\tau_o$ (Pa)	$K'$ (Pa.S <sup>n</sup> )	$n'$
Ketchup (Without nanofiber)	6.00, 5.95, 6.02	5.43, 5.41, 5.41	0.50, 0.50, 0.50
Ketchup (including 0.25 % gelatin nanofiber)	22.44, 22.51, 22.40	7.11, 7.20, 7.12	0.29, 0.28, 0.31
Ketchup (including 0.5 % gelatin nanofiber)	25.09, 25.11, 25.11	9.51, 9.51, 9.53	0.15, 0.13, 0.13

## APPENDIX D

**Table D.1:** Serum separation (%) of Gelatin nanofiber added ketchup samples after 7<sup>th</sup> day.

Gelatin nanofiber added (%)	Temperature	Serum separation (%) by centrifugal force 2200 g		Serum separation (%) by centrifugal force 5000 g	
0%	4°C	5.98	6.32	7.91	7.85
	25°C	6.91	7.54	9.67	9.50
0.25%	4°C	2.34	1.97	7.23	7.38
	25°C	2.73	3.01	7.90	7.81
0.5%	4°C	0.49	1.04	5.55	5.68
	25°C	1.10	1.52	5.83	5.70

**Table D.2:** Serum separation (%) of Gelatin nanofiber added ketchup samples after 14<sup>th</sup> day.

Gelatin nanofiber added (%)	Temperature	Serum separation (%) by centrifugal force 2200 g		Serum separation (%) by centrifugal force 5000 g	
0%	4°C	6.62	6.73	8.7	8.06
	25°C	7.01	7.73	8.92	8.88
0.25%	4°C	2.37	2.00	7.50	6.92
	25°C	2.61	3.04	7.64	7.6
0.5%	4°C	0.92	1.43	5.83	6.05
	25°C	1.33	1.85	5.95	6.02

**Table D.3:** Serum separation (%) of Gelatin nanofiber added ketchup samples after 21<sup>th</sup> day.

Gelatin nanofiber added (%)	Temperature	Serum separation (%) by centrifugal force 2200 g		Serum separation (%) by centrifugal force 5000 g	
0%	4°C	7.04	6.40	7.87	7.91
	25°C	7.00	6.91	9.76	8.93
0.25%	4°C	1.8	2.06	6.94	7.12
	25°C	3.10	2.54	7.66	8.18
0.5%	4°C	0.56	0.84	5.14	5.00
	25°C	2.06	1.45	6.01	5.84



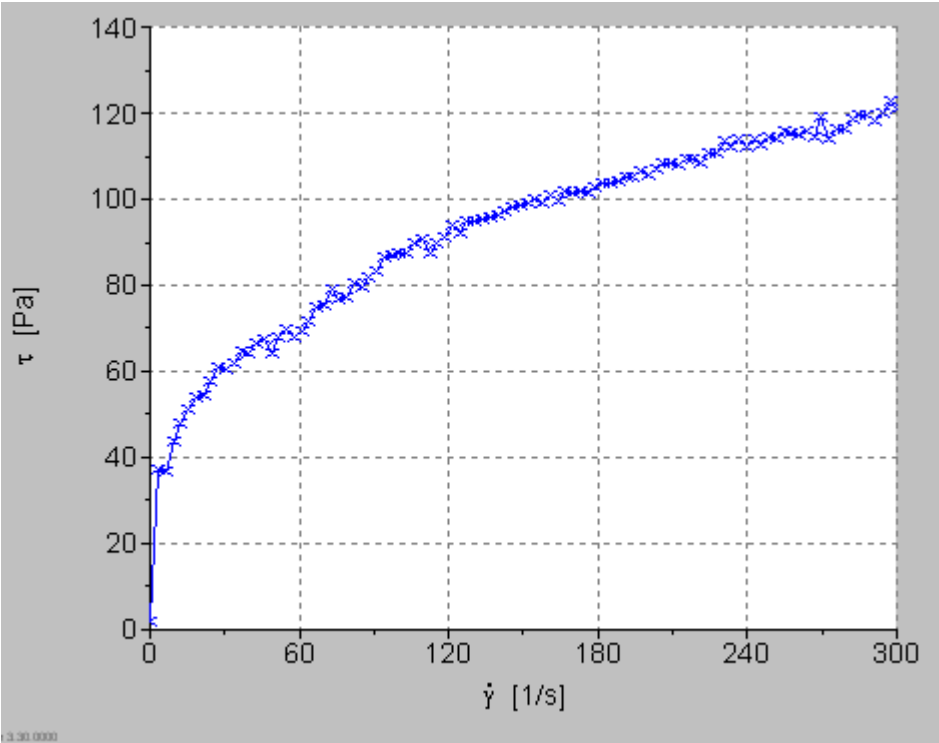
**Table D.4:** Serum separation (%) of Gelatin nanofiber added ketchup samples after 28<sup>th</sup> day.

Gelatin nanofiber added (%)	Temperature	Serum separation (%) by centrifugal force 2200 g		Serum separation (%) by centrifugal force 5000 g	
0%	4°C	6.30	5.80	8.31	7.64
	25°C	7.40	6.02	8.51	8.95
0.25%	4°C	1.9	2.4	6.35	7.09
	25°C	2.3	3.01	7.13	6.92
0.5%	4°C	0.75	0.89	5.87	5.53
	25°C	1.70	1.45	8.31	7.64

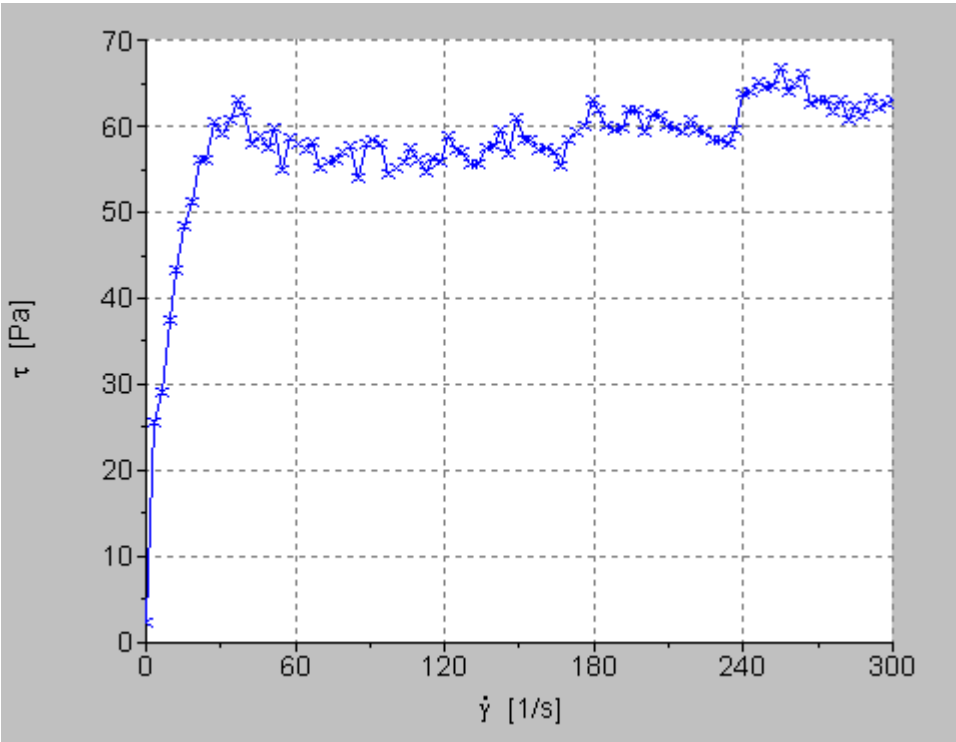
**Table D.5:** Serum separation (%) of Gelatin + CA nanofiber added ketchup samples after 7<sup>th</sup> day.

Gelatin + CA nanofiber added samples (%)	Temperature	Serum separation (%) by centrifugal force 2200 g		Serum separation (%) by centrifugal force 5000 g	
0.5%	4°C	0.46	0.62	1.53	2.10

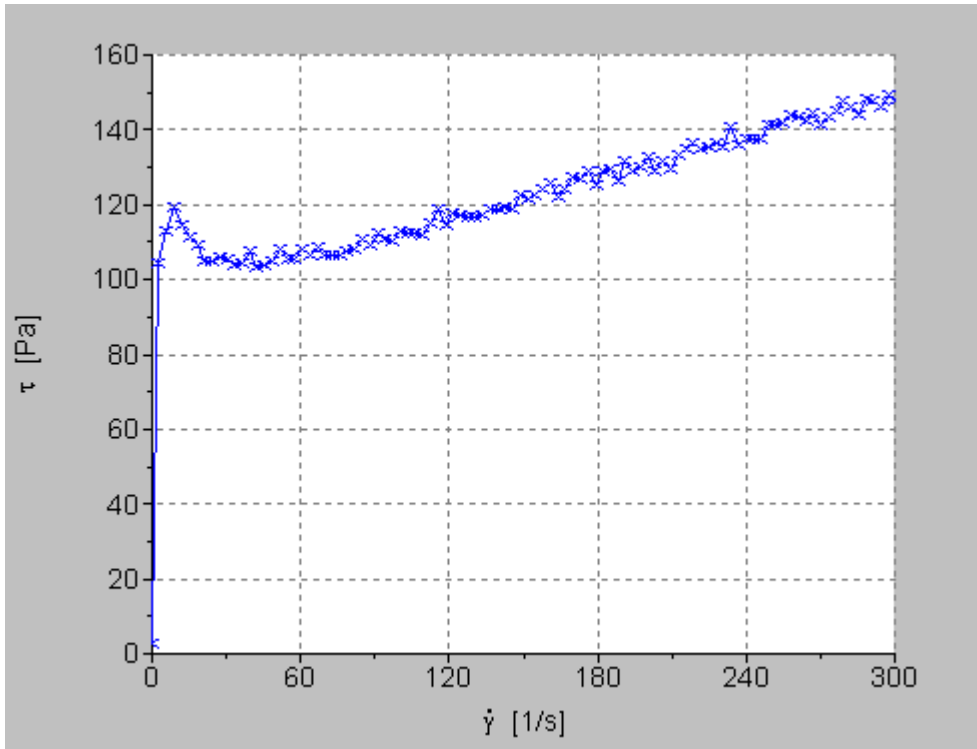
**APPENDIX E:**



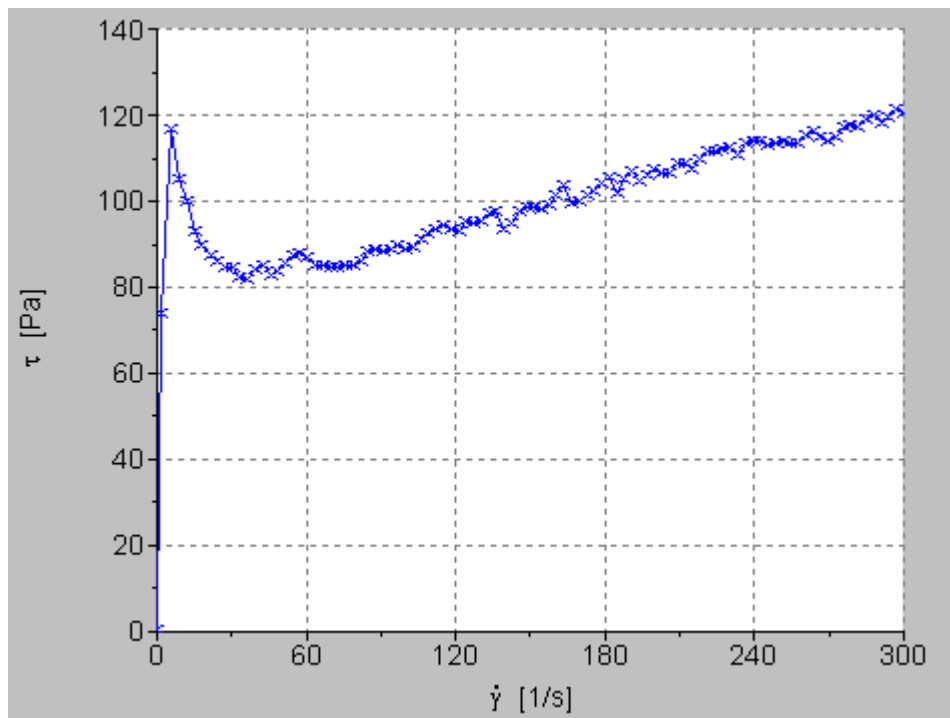
**Figure E.1:**Ketchup without nanofiber 4°C 7<sup>th</sup> day.



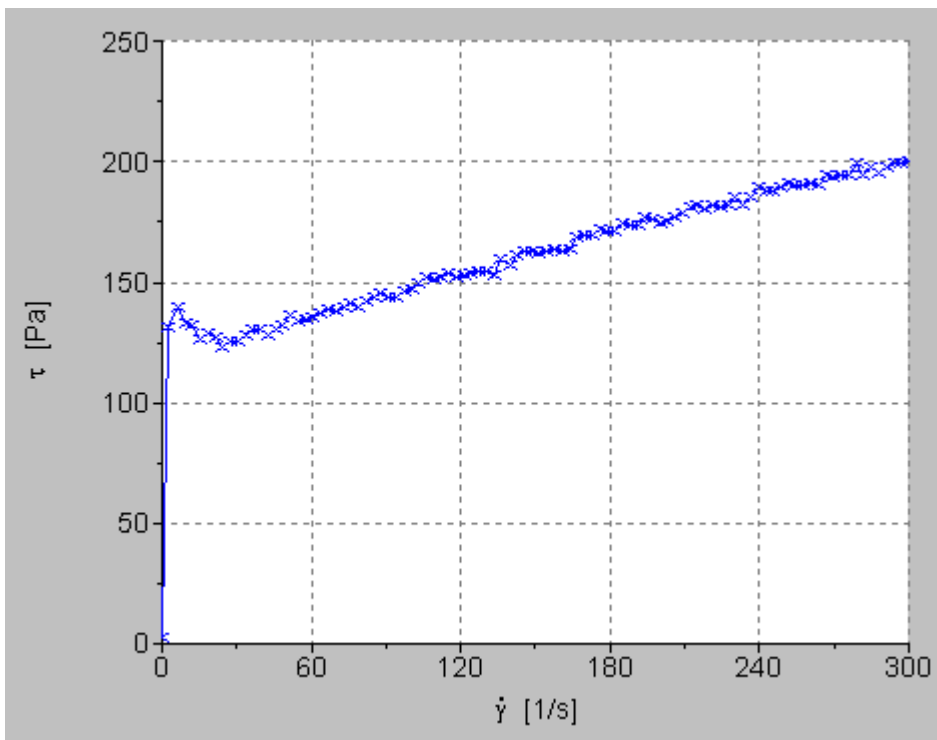
**Figure E.2:**Ketchup without nanofiber 25°C 7<sup>th</sup> day.



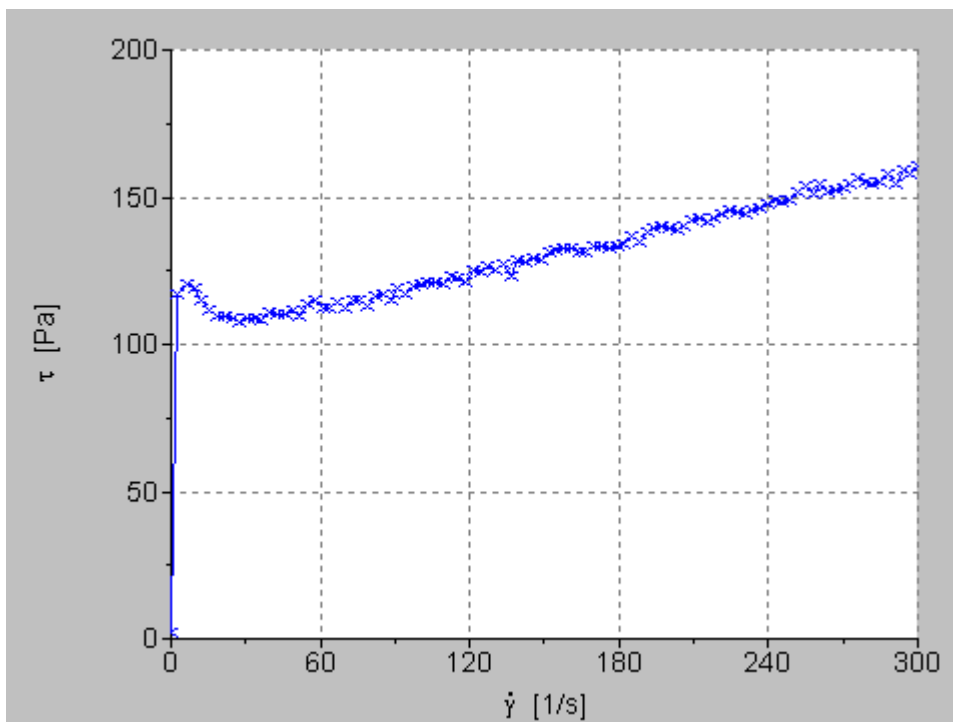
**Figure E.3:**Ketchup (including 0.25% gelatin nanofiber) 4°C 7<sup>th</sup> day.



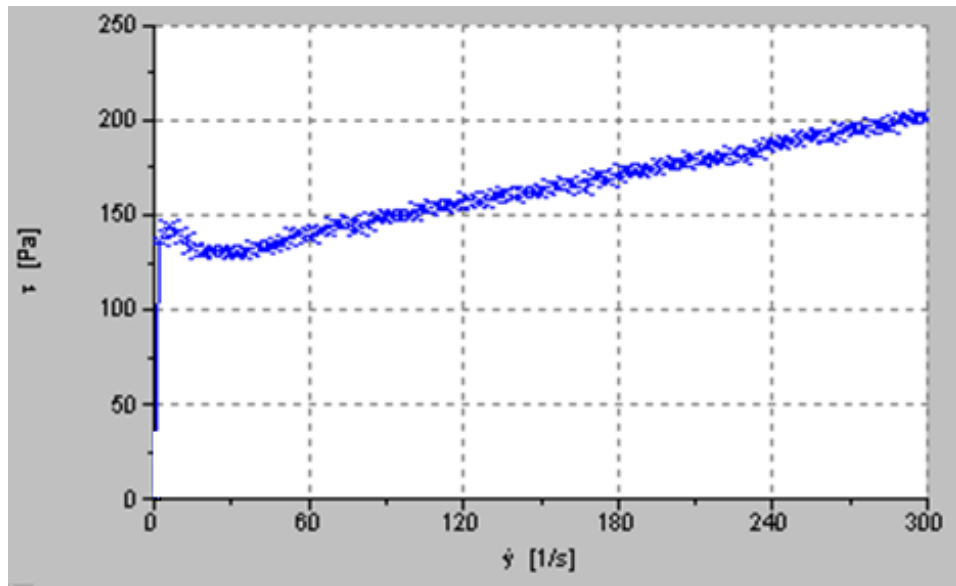
**Figure E.4:**Ketchup (including 0.25% gelatin nanofiber) 25°C 7<sup>th</sup> day.



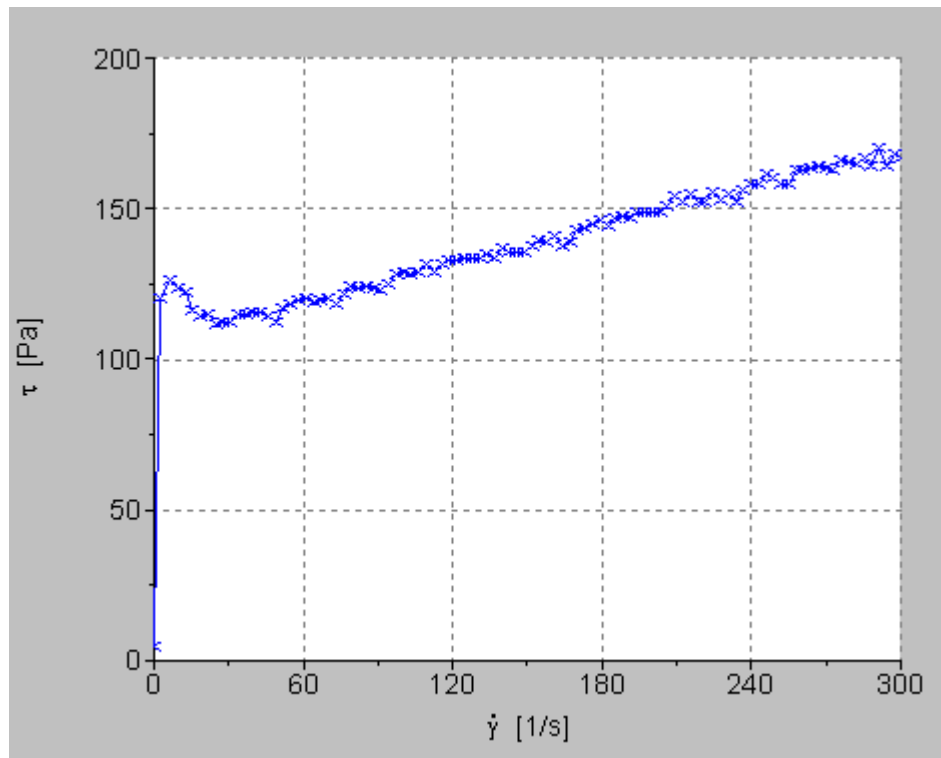
**Figure E.5:** Ketchup (including 0.5% gelatin nanofiber) 4°C 7<sup>th</sup> day.



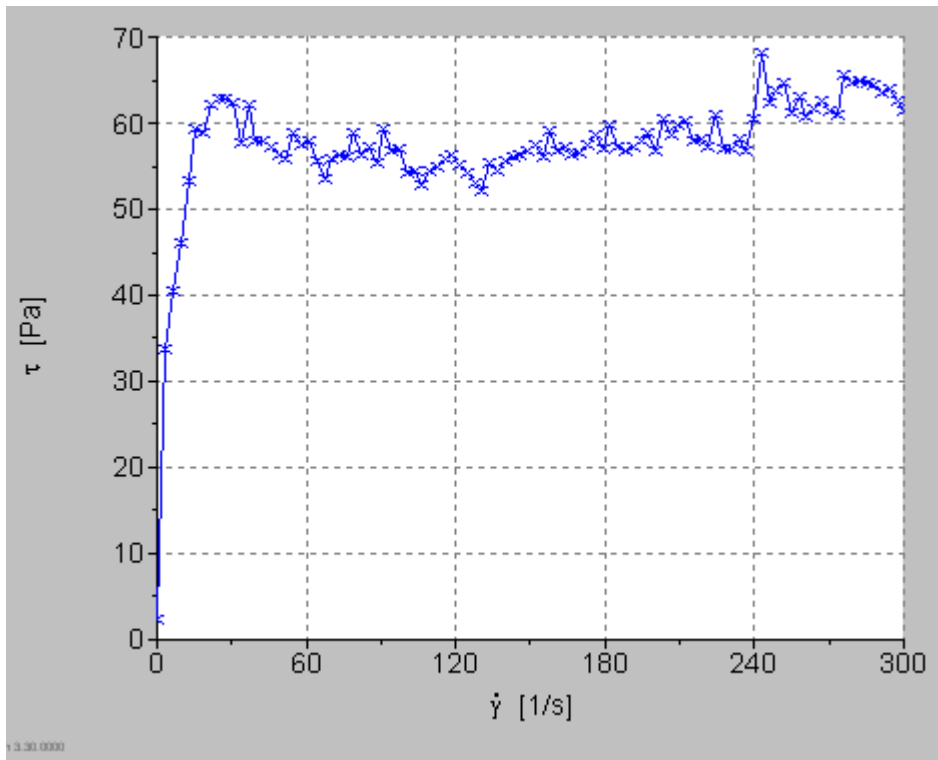
**Figure E.6:** Ketchup (including 0.5% gelatin nanofiber) 25°C 7<sup>th</sup> day.



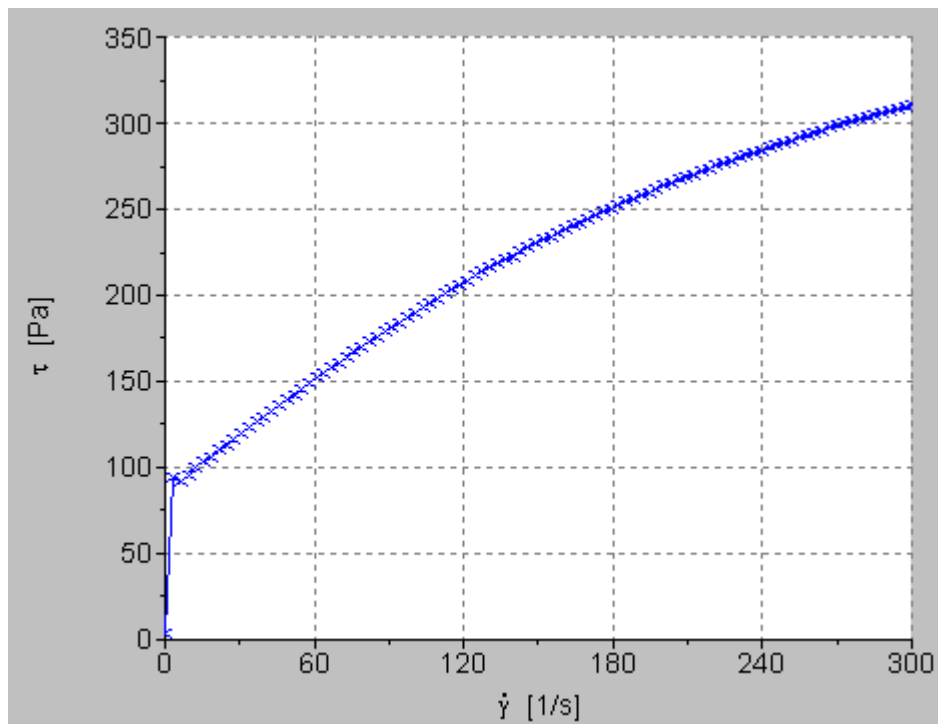
**Figure E.7:** Ketchup (including 0.5% gelatin-CA nanofiber) 4°C 7<sup>th</sup> day.



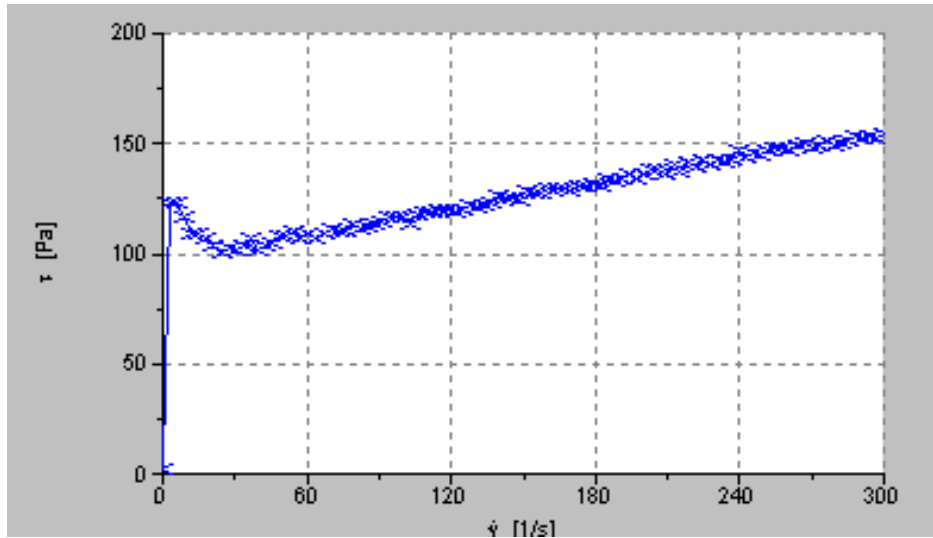
**Figure E.8:** Ketchup (including 0.5% gelatin-CA nanofiber) 25°C 7<sup>th</sup> day.



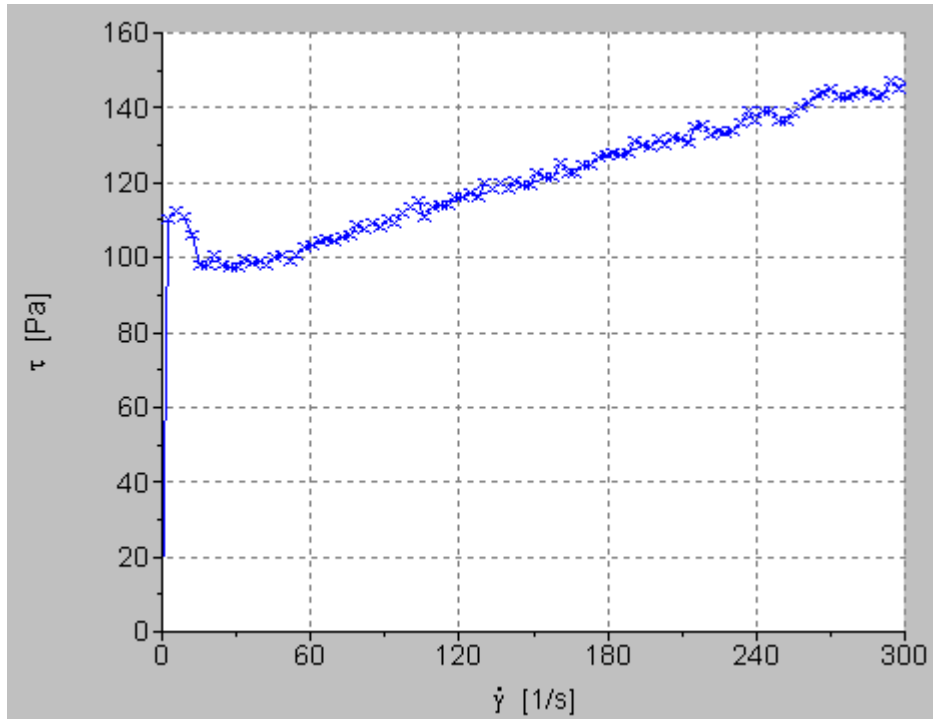
**Figure E.9:** Ketchup without nanofiber 4°C 14<sup>th</sup> day.



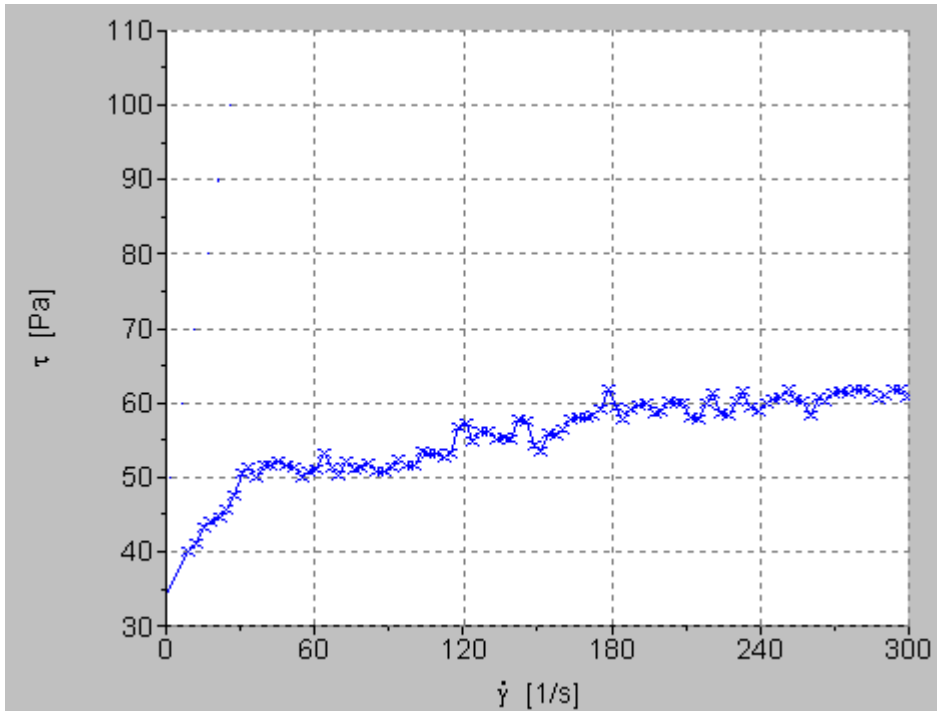
**Figure E.10:** Ketchup without nanofiber 25°C 14<sup>th</sup> day.



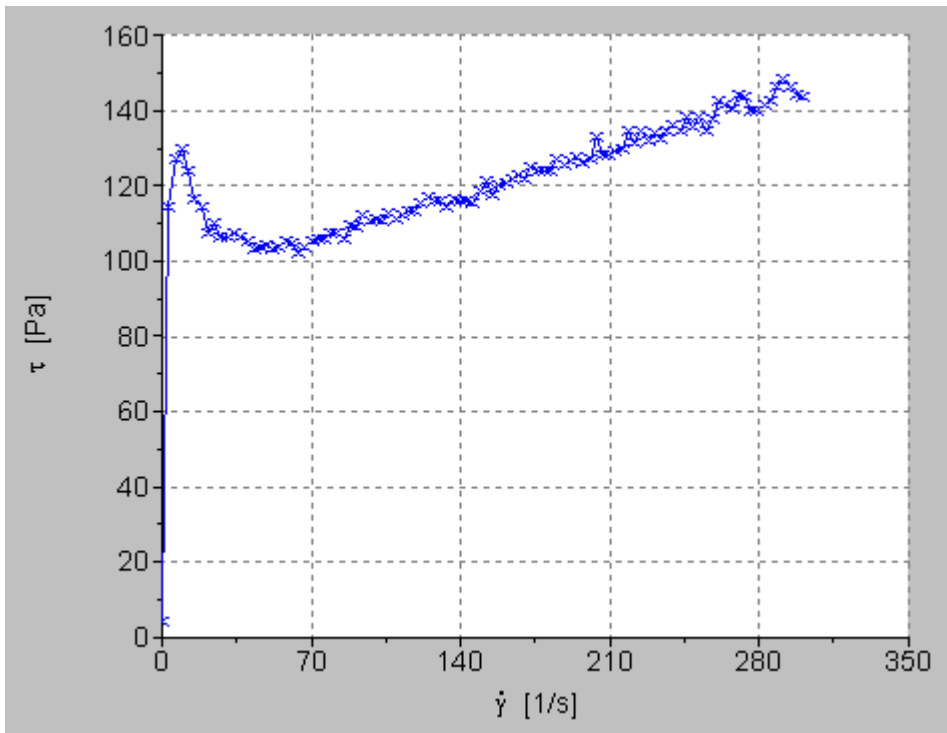
**Figure E.11:** Ketchup (including 0.25% gelatin nanofiber) 4°C 14<sup>th</sup> day.



**Figure E.12:** Ketchup (including 0.25% gelatin) 25°C 14<sup>th</sup> day.

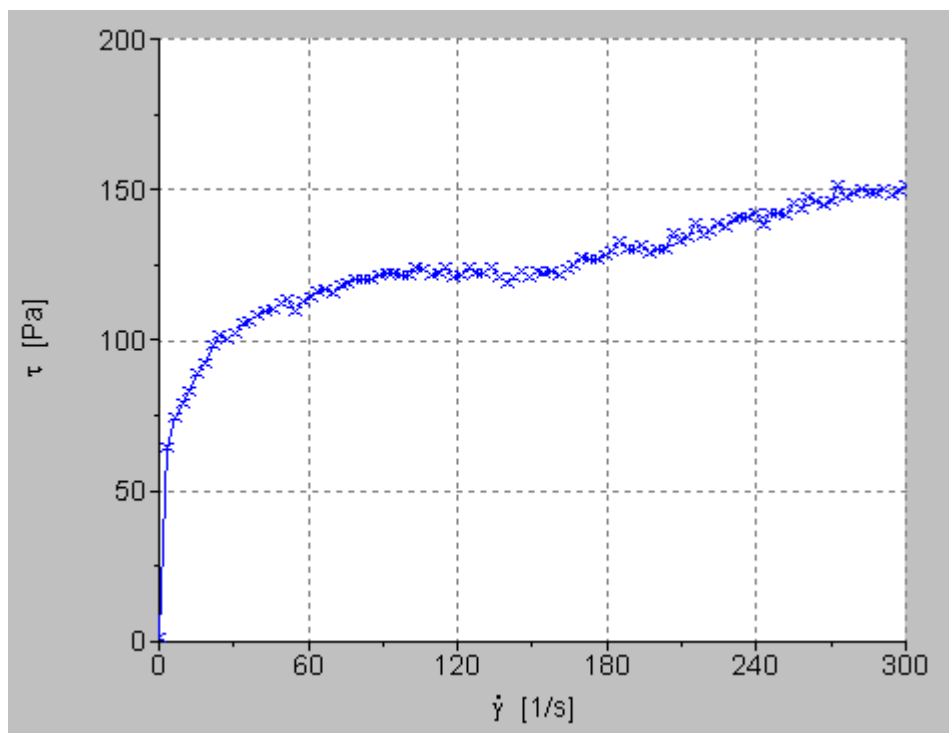


**Figure E.13:** Ketchup (including 0.5% gelatin nanofiber) 4°C 14<sup>th</sup> day.

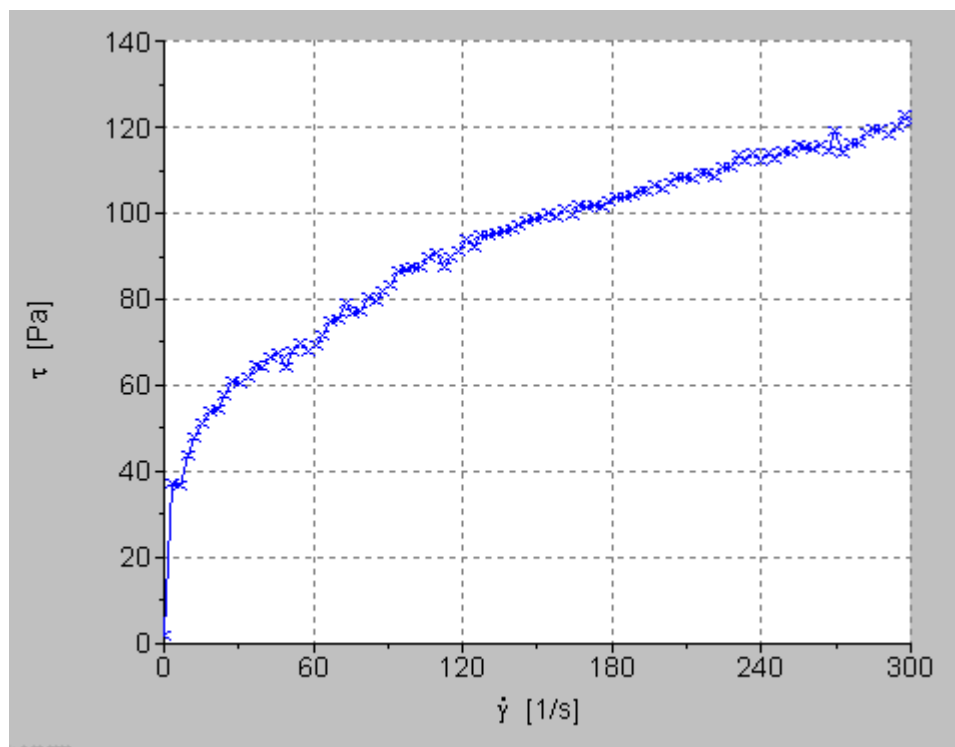


**Figure E.14:** Ketchup (including 0.5% gelatin nanofiber) 25°C 14<sup>th</sup> day.

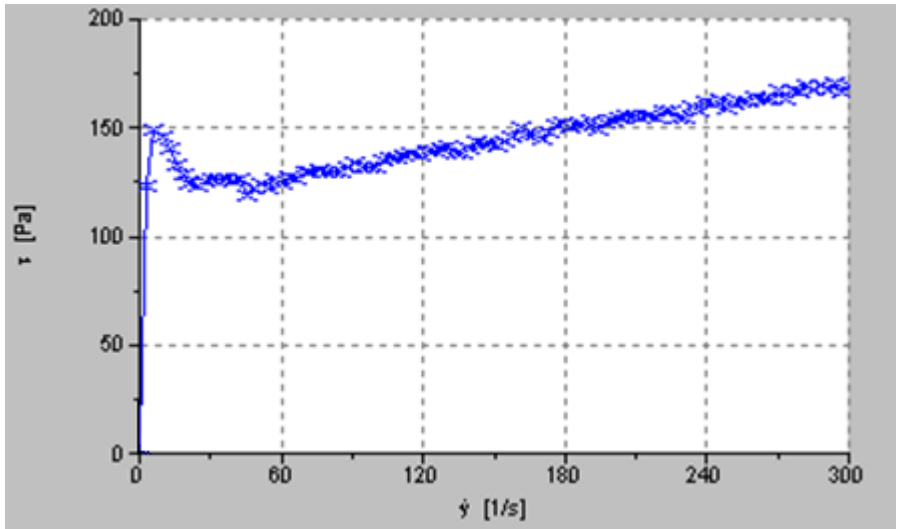




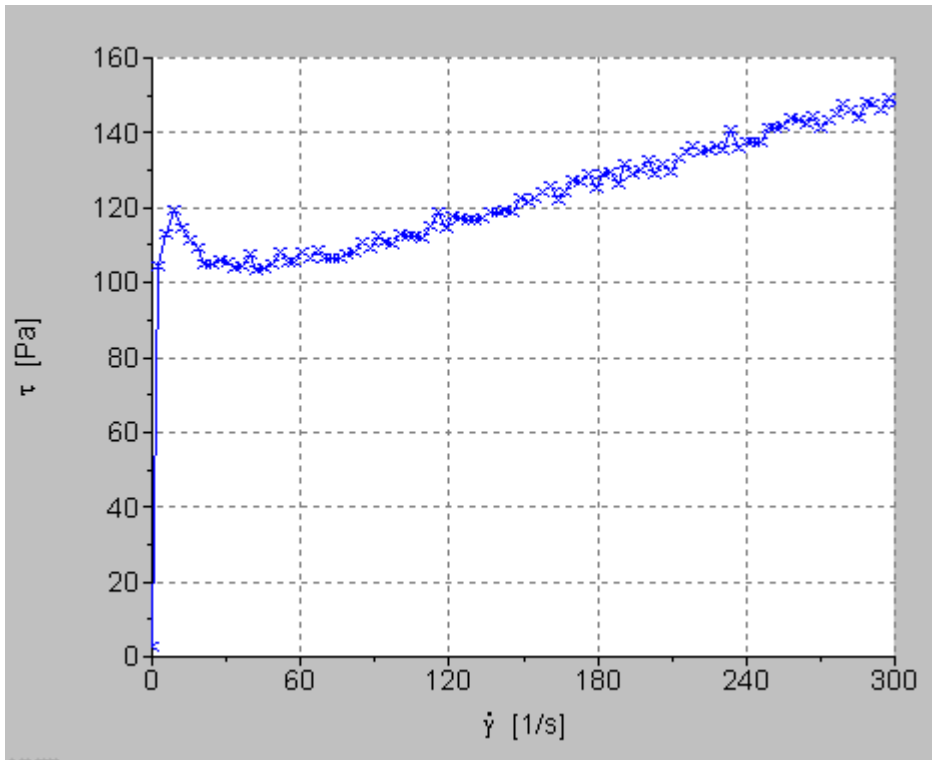
**Figure E.15:** Ketchup without nanofiber 4°C 21<sup>th</sup> day.



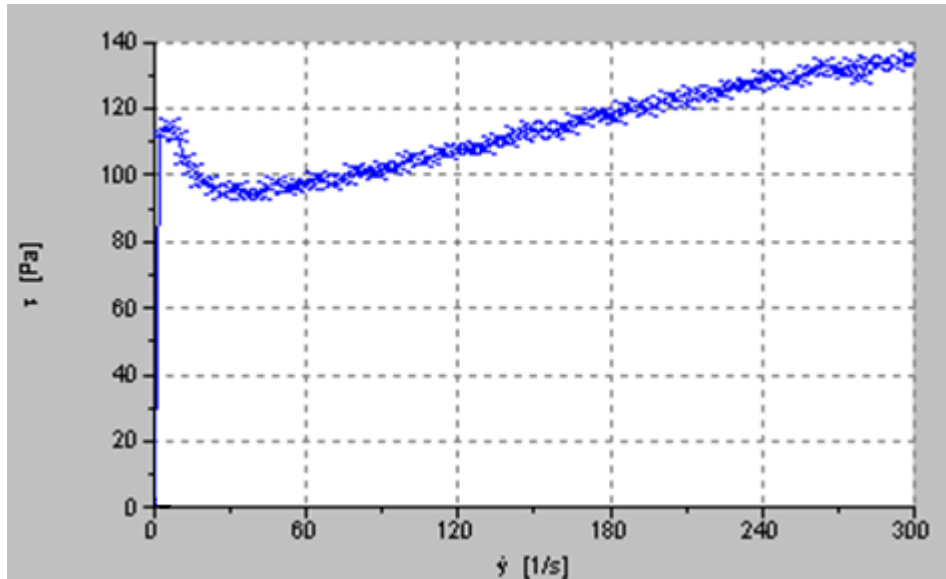
**Figure E.16:** Ketchup without nanofiber 25°C 21<sup>th</sup> day.



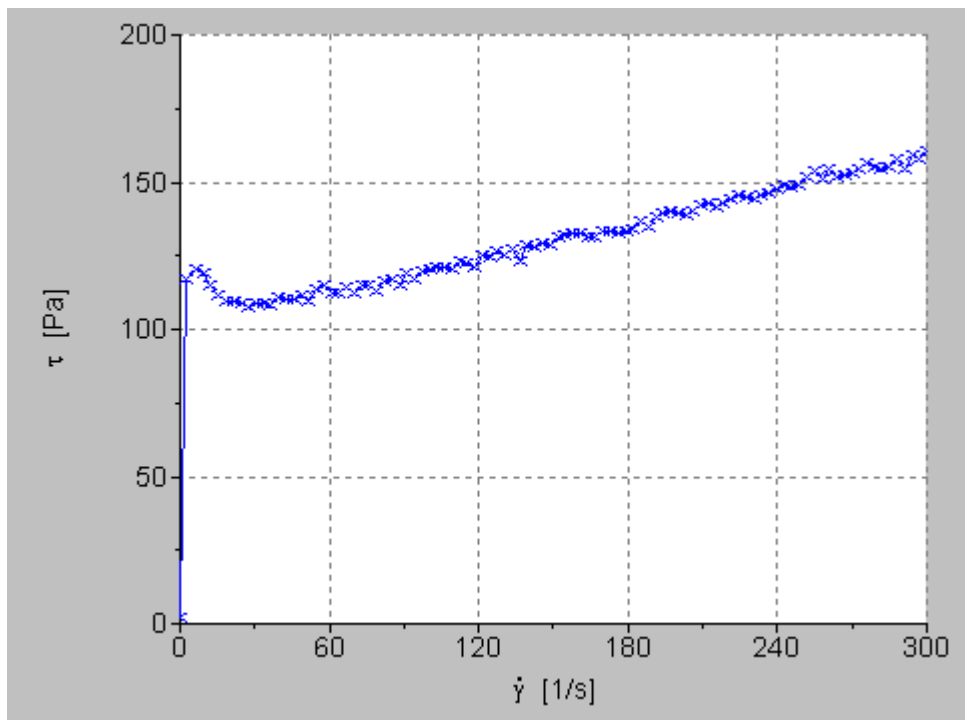
**Figure E.17:** Ketchup (including 0.25% gelatin nanofiber) 4°C 21<sup>th</sup> day.



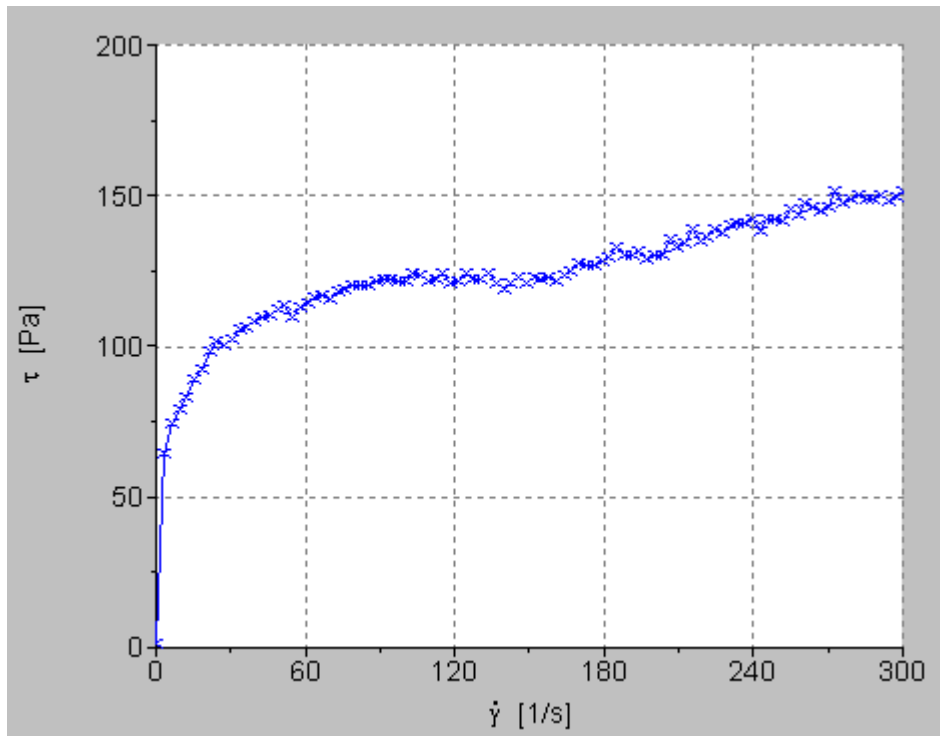
**Figure E.18:** Ketchup (including 0.25% gelatin nanofiber) 25°C 21<sup>th</sup> day.



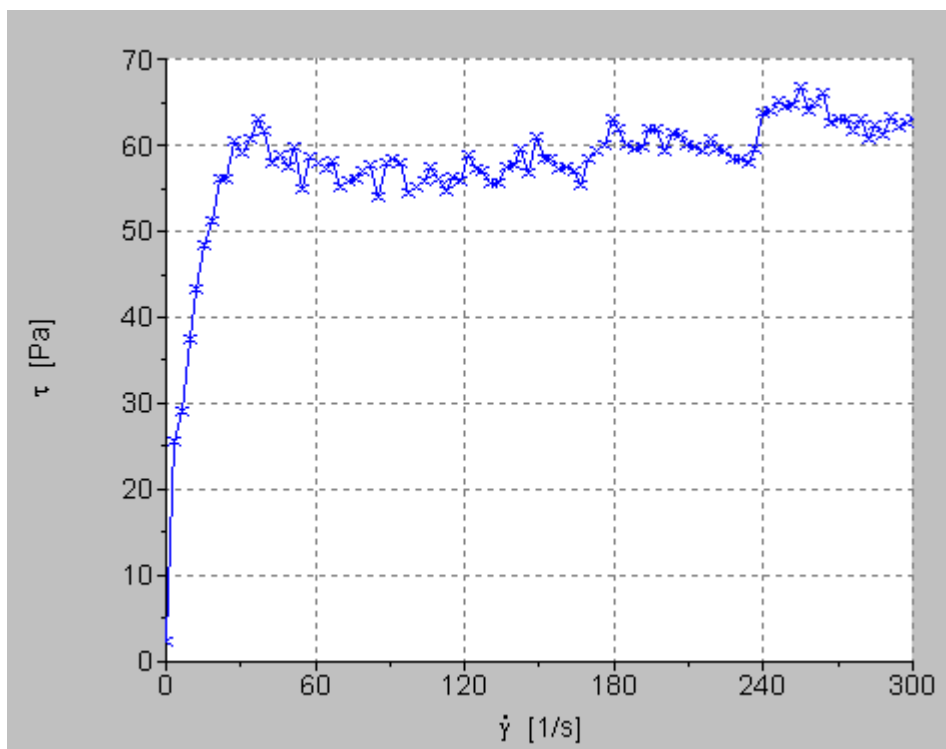
**Figure E.19:** Ketchup (including 0.5% gelatin nanofiber) 4°C 21<sup>th</sup> day.



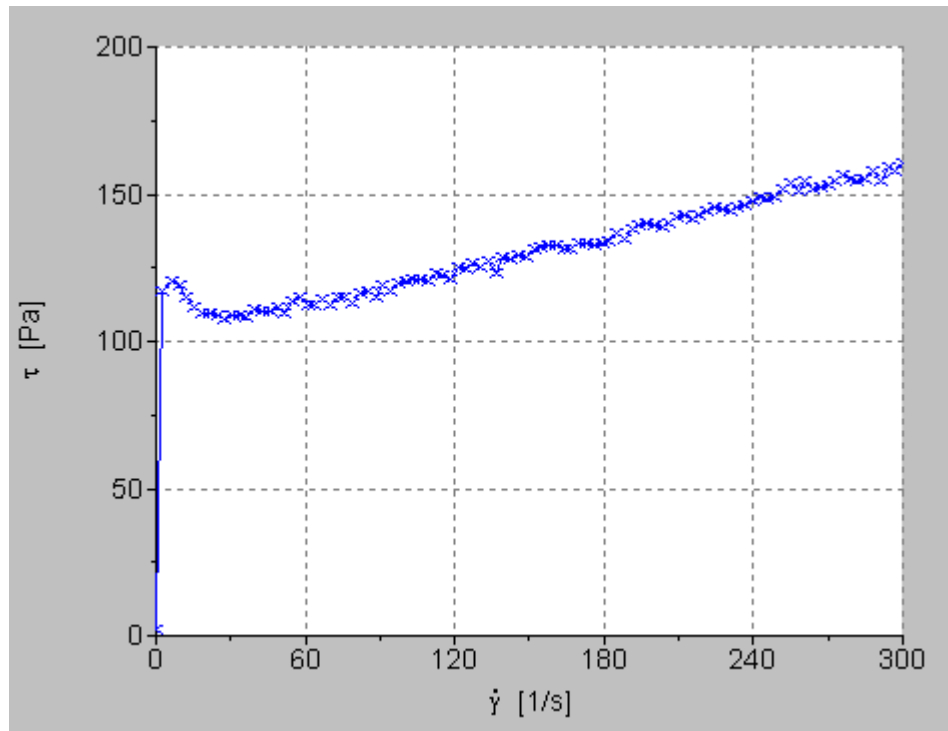
**Figure E.20:** Ketchup (including 0.5% gelatin nanofiber) 25°C 21<sup>th</sup> day.



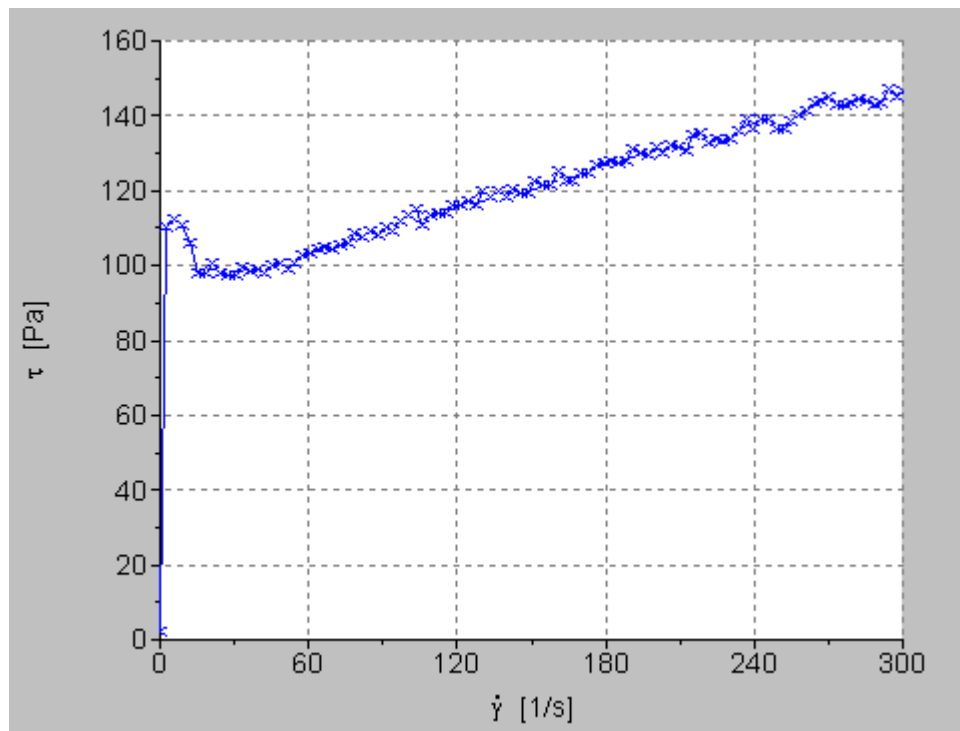
**Figure E.21:** Ketchup without nanofiber 4°C 28th day.



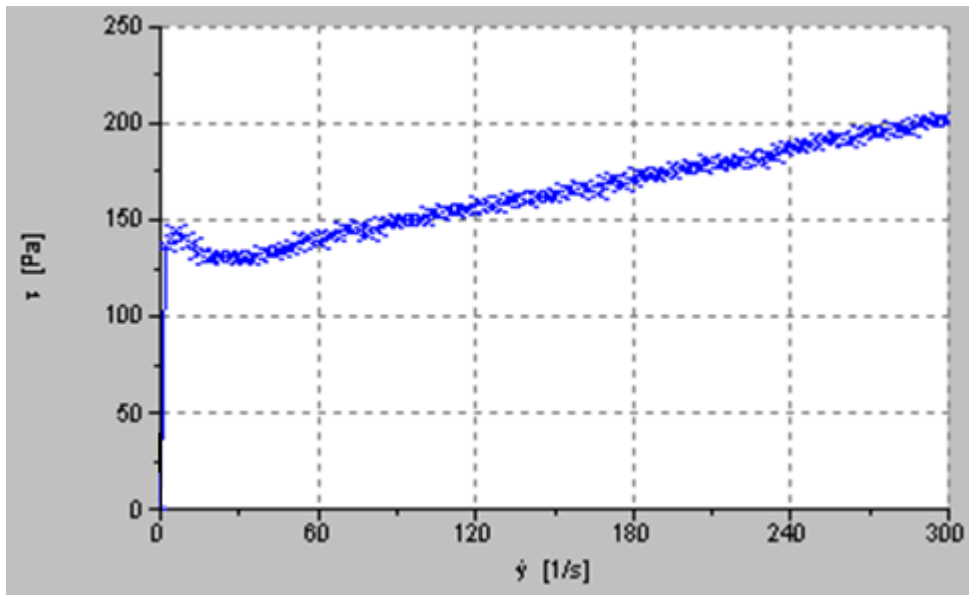
**Figure E.22:** Ketchup without nanofiber 25°C 28<sup>th</sup> day.



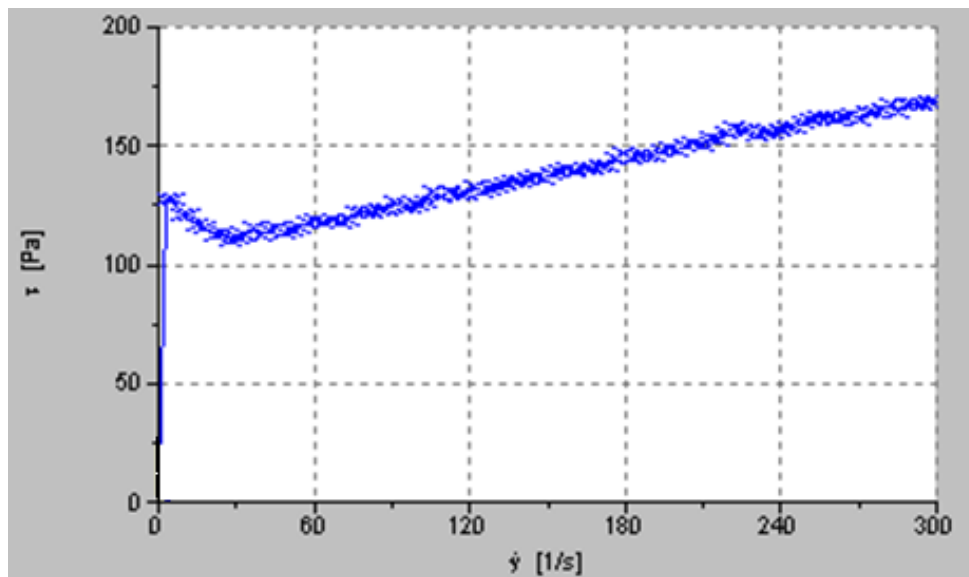
**Figure E.23:** Ketchup (including 0.25% gelatin nanofiber) 4°C 28<sup>th</sup> day.



**Figure E.24:** Ketchup (including 0.25% gelatin nanofiber) 25°C 28<sup>th</sup> day.

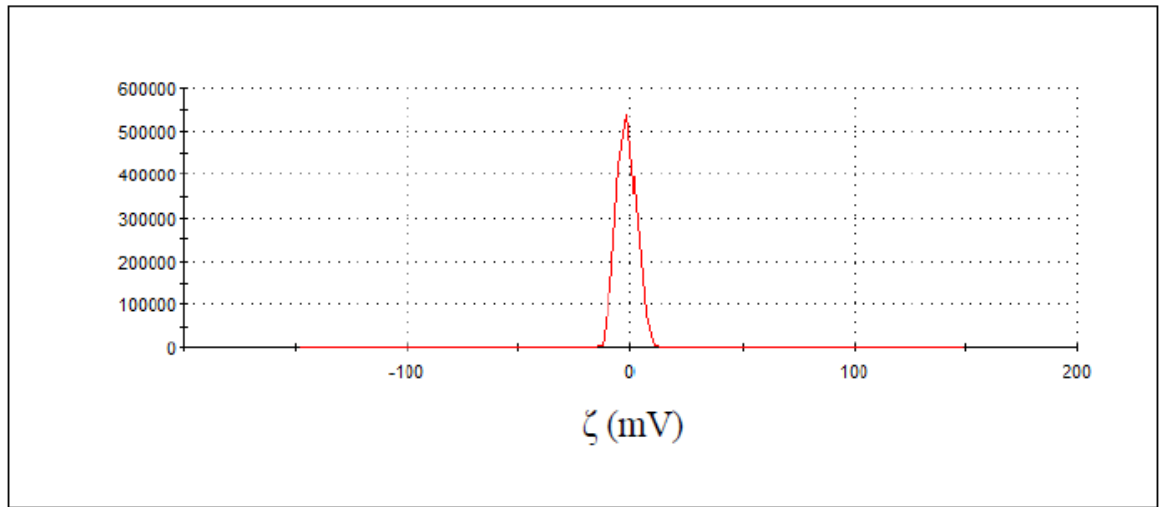


**Figure E.25:** Ketchup (including 0.5% gelatin nanofiber) 4°C 28<sup>th</sup> day.

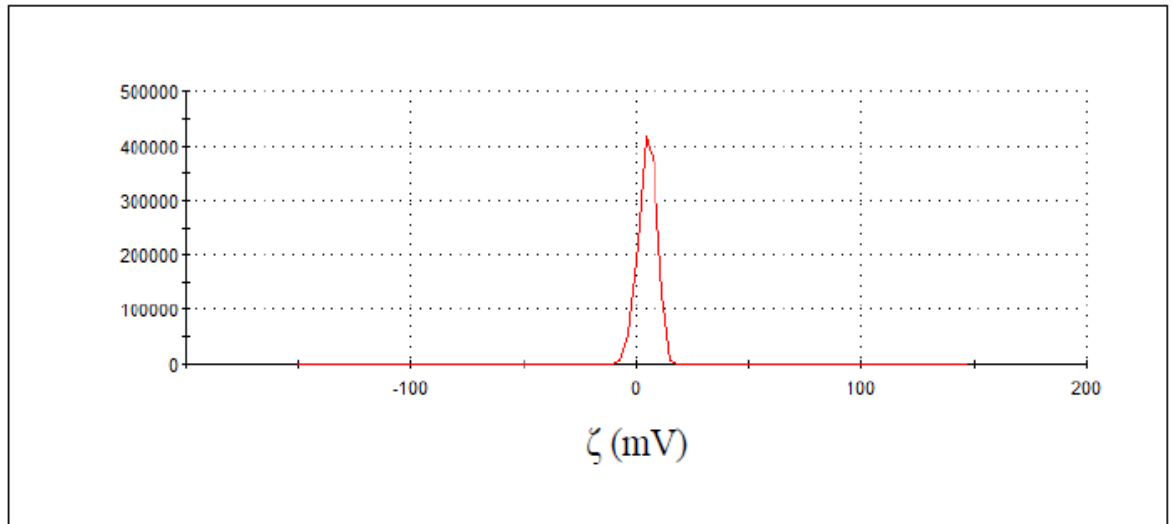


**Figure E.26:** Ketchup (including 0.5% gelatin nanofiber) 25°C 28<sup>th</sup> day.

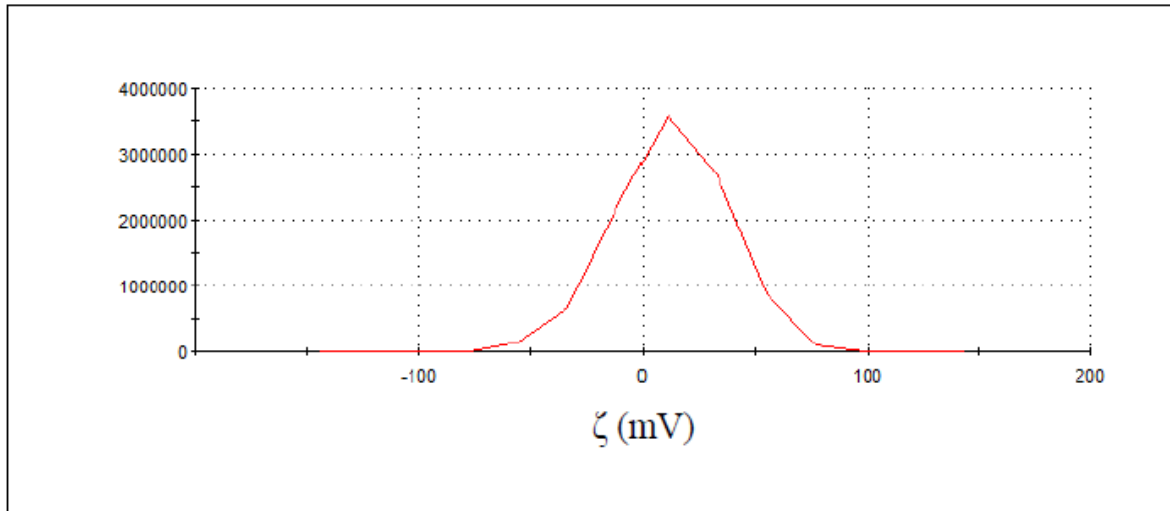
## APPENDIX F



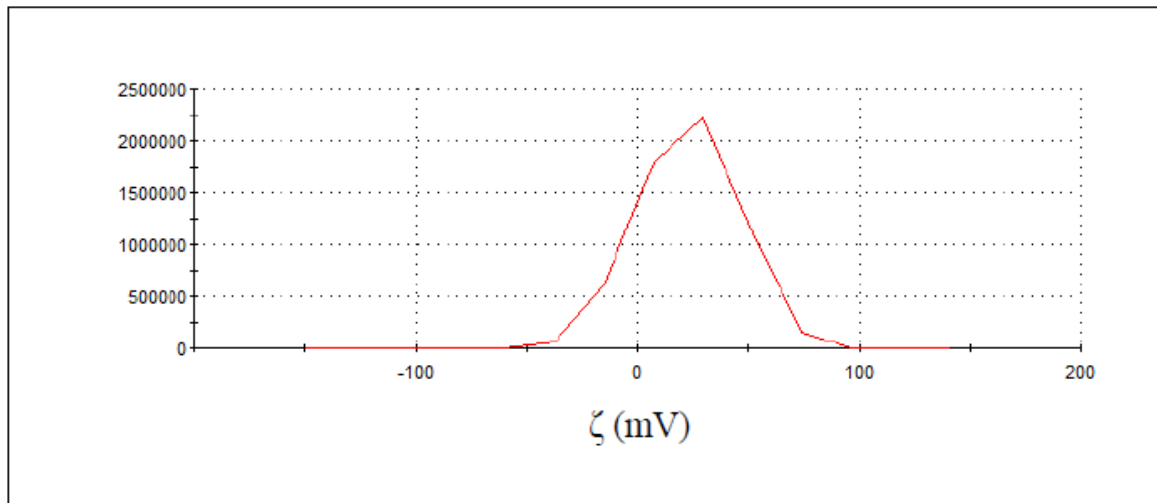
**Figure F.1:** Zeta potential curve of gelatin.



**Figure F.2:** Zeta potential curve of gelatin 7% nanofiber.



**Figure F.3:** Zeta potential curve of gelatin 20% nanofiber.



**Figure F.4:** Zeta potential curve of gelatin-CA nanofiber.



## CURRICULUM VITAE



**Name Surname:**Saman HENDESSI

**Place and Date of Birth:** Iran, 09/16/1986

**Address:** No.16, Menekşe Avenue, Çamlık Street, Hacıosman, Tarabya, Sariyer, 34457, Istanbul, Turkey

**E-Mail:** hendessi@itu.edu.tr

**B.Sc.:**

Urmia University of Agriculture Engineering, West Azerbaijan, Iran , Food Eng., Bachelor of Science (GPA: 13.60/20)

**M.Sc.:**

Istanbul Technical University of Food Engineering, Istanbul, Turkey, Food Eng., Master of Science (GPA:3.06/4)

**Professional Experience and Rewards:**

- Attend in Lund University of Food Engineering’s workshop, (5 - 18 June 2011), Lund, Sweden

**List of Publications and Patents:**

- “GelatinElectrospunNanofibers as an Emulsifier in O/W Emulsions” – Poster–*IFT Annual Meeting & Food Expo 2013* (13-16 July 2013), Chicago, IL USA.
- “Risk Evaluation of Engineered Nano Particles (ENPs) in Food Industry”\_Poster\_ *Food Micro 2012* (3-7 Septamber 2012), Istanbul, Turkey
- “Nanoparticles With Antimicrobial Activity for Food Packaging”\_Poster\_ *Food Micro 2012* (3-7 Septamber 2012), Istanbul, Turkey