

Thermal degradation of polymers and polymer blends

Polimerlerin ve polimer karışımlarının ısısal bozunması

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Review Article

ABSTRACT

Polymers and their blends undergo various thermal or radiation effects in areas of usage. Therefore, in the academic investigations and industrial applications, radiolysis and thermal degradation of polymers, polymer blends and mixed polymers is very important. In this study, recent studies on thermal degradation of heated and irradiated polymers and their blends being done by the second branch in left side of our polymer tree (Fig.1) are reviewed. The studies have been classified as preparation and investigation of graft copolymer structures with γ -rays, determination of gelation dose for γ -irradiated polymers, thermal degradation of γ -irradiated polymers, determination of thermal gelation points of polymers, comparison of various isothermal thermogravimetric methods and new compact method, and preparation and thermal degradation of maleic anhydride copolymers and terpolymers.

Key Words

Polymer, polymer blends, thermal stability, thermal degradation, radiation, thermal gelation, gelation dose, maleic anhydride, graft copolymer, terpolymer.

ÖZET

Polimerler ve polimer karışımları uygulama alanlarında çeşitli ısısal etkilere veya yüksek enerjili ışın etkilerine maruz kalırlar. Bu yüzden, akademik araştırmalarda ve endüstriyel uygulamalarda polimerlerin ve polimer karışımlarının radyolizi ve ısısal bozunması çok önemlidir. Bu çalışmada, polimer ağacımızın soldan ikinci dalı tarafından, ısıtılmış ve ışınlanmış polimerlerin ve polimer karışımlarının ısısal bozunması ile ilgili yaptıkları son çalışmalar gözden geçirilmiştir. Çalışmalar, γ -ışınları ile aşı kopolimerlerinin hazırlanması ve yapılarının incelenmesi, γ -ışınları ile ışınlanmış polimerlerin jelleşme dozunun belirlenmesi, γ -ışınları ile ışınlanmış polimerlerin ısısal bozunması, polimerlerin ısısal jelleşme noktasının belirlenmesi, çeşitli izotermal termogravimetrik yöntemlerin kıyaslanması, bu alanda yeni bir yöntem önerilmesi, maleik anhidrit kopolimer ve terpolimerlerin hazırlanması ve ısısal bozunması olarak sınıflandırılmıştır.

Anahtar Kelimeler

Polimer, polimer karışımları, ısısal kararlılık, ısısal bozunma, ışın, ısısal jelleşme, jelleşme dozu, maleik anhidrit, aşı kopolimeri, terpolimer.

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INTRODUCTION

Heat and radiation effects are very important for chemical processing applications in several industries. When polymers are heated or irradiated, they give positive ions, free radicals, and excited molecules. A wide range of reactive species become available; they can be used as an origin for heat and radiation-initiated reactions such as modification, chain scission, crosslinking, or degrading materials.

Heat and radiation-initiated reactions can be classified as two types: (1) crosslinking and scission and (2) grafting and curing. Crosslinking is intermolecular bond formation of polymer chains. The degree of crosslinking is proportional to the heating rate and radiation dose. Crosslinking during irradiation sometimes does not require unsaturated or other more reactive groupings, but having unsaturation and reactive groups on polymer chain makes the initiation of thermal degradation reaction, easier. The mechanism of crosslinking generally varies with the polymers concerned. The universally hydrogen atom, followed by abstraction of a second hydrogen atom from a neighbouring chain to produce molecular hydrogen. Then two adjacent polymeric radicals combine to form a crosslink. Chain scission is the opposite process of crosslinking in which the rupturing of C-C bonds occurs. Crosslinking increases the average molecular weight, but chain scission process reduces it. If the amount of the heat or radiation dose is enough, chain breaking occurs through the cleavage of C-C bond [1]. The crosslinking of polymers during heating or radiation is most desirable reaction and can be enhanced by addition of small amount of molecules called as crosslink promoters or co-agents. The final changes of polymer during heating and irradiation are rather complex. There have always been competing reactions of crosslinking and main chain scission simultaneously.

The aim of heating and radiation processing of polymers is to modify their physical and chemical properties by using heat energy and ionizing radiation for improving their properties in order to add value. The industrial applications

of heating processing in polymer industry are very important in terms of the knowing of thermal behavior of polymer before any application.

There are lots of advantages of both radiation and heating technologies. Some of these can be counted as no catalyst requirements for the reactions, no contamination due to the chemical initiator or modifiers, sustainable reaction rates at lower temperatures for radiation and in any phase, etc. Radiation and heating processing used to be applied in lots of industrial areas such as biomedical, textile, electrical, membrane, cement, coating, rubber, aerospace and pharmaceutical industries.

The first investigations on the influence of high energy irradiation and heating processing on the thermal stability of polymers had been nearly started by Professor Olgun Güven and co-workers in Turkey. Therefore, in this review, it has been focused primarily on the studies of Professor O.Güven and S. Basan who is being the first PhD student about radiation technology applications and thermal degradation of polymers. There are four kinds of studies on investigating various properties of polymers and their blends. The preparation and investigation of graft copolymer structures with γ -rays, determination of gelation point of an irradiated and heated polymer and investigation of thermal degradation of polymers, polyblends, maleic anhydride copolymers, and terpolymers.

The Preparation and Investigation of Graft Copolymer Structures with γ -Rays

First doctorate thesis supervised by O.Güven was about the effect of composition on the thermal stability of vinyl acetate/vinyl chloride graft copolymers [2]. In this study, in order to improve the thermal stability of poly(vinyl chloride) (PVC), different amounts of vinyl acetate have been grafted onto PVC main chain. Grafting was performed by using γ -rays and according to mutual irradiation technique and for grafts having 8%, 25%, 42%, 60% and 96% of poly(vinyl acetate) (PVAc). Grafting yields have been determined gravimetrically and also followed by IR spectroscopy.

In the second study, grafting of vinyl acetate in bulk to PVC has been studied in air and vacuum [3]. Grafting was performed by using γ -rays and according to mutual irradiation technique. The PVC films immersed in monomer have been irradiated at three different dose rates, grafting ranging from 0% to 96% of PVAc have been obtained. Grafting yields have been determined gravimetrically and also followed by IR spectroscopy. In another study, the structure of vinyl acetate/vinyl chloride graft copolymer has been investigated by spectrophotometric methods[4].

Dynamic thermograms and the derivatives of the thermal degradation reactions of PVC, PVAc and graft copolymers showed that degradation takes place in two steps. From qualitative analysis of these curves, it was found that, at the beginning of degradation, the stability of all grafted samples increased over that of PVC, at higher conversion. However, 25% and 42% grafts showed less stability [5]. For quantitative analysis of thermogravimetry (TGA) curves, activation energies of thermal degradation reaction of pure PVC and grafted samples have been determined according to Freeman-Carroll method.

Isothermal thermograms of grafted samples between 230-270°C have been evaluated according to Madorsky, general rate equation and Flynn methods and the activation energies of thermal degradation reaction have been determined for pure PVC, PVAc and grafted samples [6].

To clarify the effect of the presence of PVAc on the thermal stability of PVC, mechanical mixtures of PVC and PVAc have been prepared with the same composition as the grafted samples and then degraded isothermally. It was found that PVAc, even in mixed form, increases the stability of PVC slightly. These results showed that the main reason of achieving thermally stable PVC was the chemical bonding of PVAc chains onto the main PVC chains.

The behaviors of original and thermally degraded PVC and grafted samples have been also followed by UV-VIS spectroscopy. From dynamic

and isothermal thermogravimetric results, it has been found that 25% and 42% grafts are the least stable samples among the grafts. From the UV-VIS spectrum of these samples, it was observed that they contain maximum amounts of residual double bonds. Thus, their thermal instabilities have been referred to the presence of these residual double bonds[7].

Furthermore, the effect of γ -rays on the thermal degradation of vinyl acetate/vinyl chloride graft copolymers has been investigated [8].

The Determination of Gelation Dose of γ -Irradiated Polymers

First two articles of O. Güven and co-workers are on the spectrophotometric determination of gelation dose in the γ -irradiation of PVC and PVAc. In these studies, gelation dose was defined as the minimum dose required for the formation of insoluble networks upon irradiation of polymers by ionizing radiation. Because of viscometric and solubility methods are time consuming and polymer discoloring methods, in crosslinking upon irradiation, the gelation doses have been determined by spectrophotometric methods [9,10]. It was shown that for γ -irradiated PVC, the onset of gelation could be determined spectrophotometrically. The reliability of the method has also been checked by viscometric and solubility methods.

The Thermal Degradation of γ -Irradiated Polymers

The thermal degradation of unstabilized PVC and PVAc irradiated with γ -rays has been investigated by dynamic thermogravimetry in nitrogen atmosphere [11,12]. The overall effect of irradiation is to render PVC more susceptible to thermal degradation. The change in activation energy of degradation with dose showed a behavior parallel with the change of intrinsic viscosity ($[\eta]$) with dose. The minimum and maximum E_A values have been found to correspond with the minimum and maximum observed on $[\eta]$ versus dose curves. This behavior indicates an inverse relationship between the rate of thermal degradation and molecular size.

In other study, the thermal stability of the gel

and sol fractions of PVAc irradiated with gamma-rays in various doses in the post-gel region has been investigated by dynamic thermogravimetry. It has been found that the gel fractions were more stable than the sol fractions and the thermal stability of gamma-irradiated bulk PVAc lied between those of the gel and sol fractions. However, increasing amounts of gel did not improve the thermal stability of PVAc irradiated in high doses [13].

The Determination of Thermal Gelation Points of Polymers

In the first study of this section, the thermal gelation points of a vinylidene chloride/acrylonitrile random copolymer have been determined using a spectrophotometric technique [14]. In the first part, the thermal gelation temperature and the thermal gelation weight loss have been determined as 219°C and 4.6%, respectively. In the second part, isothermal gelation times at 150, 160, 170 and 180°C have been determined as 256, 105, 44 and 27 min, respectively. At these temperatures, the isothermal gelation weight losses have been found to be 0.37, 0.68, 0.92 and 1.26%, respectively. In conclusion, it has been shown that the crosslinking reaction in vinylidene chloride/acrylonitrile copolymer began at lower temperatures and lower weight losses in isothermal heating than those of in dynamic heating.

In the second study of this section, the dynamic and isothermal gelation points of PVC have been determined using spectrophotometric and viscometric techniques [15]. Four different PVC samples, with viscosity-average molar masses of 70000, 90000, 106000 and 141000, have been used. The dynamic thermal gelation points of PVC samples heated to temperatures between 120 and 280°C have been found to be between 232 and 236°C. Isothermal gelation times of PVC ($M_v = 106000$) heated at 170, 180, 190 and 200°C have been determined as 345, 177, 78 and 37 min., respectively. An inverse relationship between the tendency to dynamic and isothermal gelation with increase in molar mass of PVC samples has been found. On the other hand, the tendency to isothermal gelation of PVC increases with raising temperature.

In the third study, preheating between the temperatures of 200 and 280°C was applied to a film-structured PVC sample, which has a gelation temperature about 250°C. After this preheating, PVC's thermomechanical and thermal differences at the temperatures before and after thermal gelation, were observed. Consequently, some thermomechanical and thermal parameters obtained at these temperatures were compared. It could be said to be an easier method to determine the gelation temperature of a polymer [16].

Comparison of Various Isothermal Thermogravimetric Methods and New Compact Method

In the first study, various isothermal methods of thermogravimetric analysis have been applied for degradation of PVC [17]. The kinetic parameters such as the reaction order, activation energy and pre-exponential factor have been evaluated according to existing differential and integral methods of analysis. The major drawbacks and advantages pertaining to five different methods have been pointed out and discussed.

In the second study, a new method for determination of kinetic parameters from isothermal weight loss curves was proposed [18]. By applying this compact method, it is possible to follow the change in reaction order with temperature and the dependence of activation energy on extent of the reaction by using a single diagram. The values of the kinetic parameters determined by this method are in very good agreement with the values obtained by various other thermogravimetric analysis methods.

Thermal Degradation of Polymer and Their Blends

There are various studies owing to the second branch in left side of our polymer tree (Figure 1). The first group of them is on thermal degradation of polymer blends and the other group is the preparation and thermal degradation of maleic anhydride copolymers and terpolymers. The first study in this group is thermal degradation of polymer blends of PVC with poly(tetramethylene sebacate)[19]. In this work, the thermal degradation of PVC-PTMS blends has been studied over the whole composition range, using thermal

volatilisation analysis (TVA) and thermogravimetry (TG). In TVA studies, degradation products have been separated and investigated and in the TG experiments, both isothermal and temperature programmed conditions have been used. It has been found that these blends were homogeneous over most of the composition range when casted as films from solution. Powder mixtures of two polymers showed no evidence of interaction during degradation, but in the case of film blends, the PVC was stabilised at low to moderate PTMS contents and destabilised at very high PTMS concentrations. There was an increase in the residue of degradation at 500°C, in most of the blends. The interactions were explained in terms of reaction of chlorine chain carriers in PVC dehydrochlorination with methylene groups in the PTMS, followed by crosslinking of macroradicals.

In the second study, the thermal degradation of PVC/polydimethylsiloxane (PDMS) blends has been studied by TG over the whole composition range and by TVA for 1:1 (by weight) blends [20]. From the TG data, curves have been constructed to enable the experimental weight loss behaviour to be compared with that of expected for the

composition in the absence of any effects due to mixing. The results showed destabilisation at low loadings of PDMS for degradations at atmospheric pressure, but for compositions with 50% or more PDMS, both polymers were stabilised, particularly the PDMS, which shows much slower weight loss than expected when 10% PVC is present. Degradation products in TVA experiments have been separated and investigated: there are no new volatile products in the case of the blends. An interpretation of the reasons for the observed effects is presented.

In the third study, the thermal degradation of blends of PVC with bisphenol A, polycarbonate has been studied by TG and TVA [21]. In the TG experiments, both programmed heating and isothermal heating (at 280°C) have been used and the full composition range from PVC to polycarbonate has been examined. In TVA experiments, blends of equal weights of the polymers have been employed and both the volatile and tar/wax fractions of products have been studied. As initial separation of the volatile product fraction by subambient TVA has been used to assist product identification, which has been based on IR and MS methods. In degradation of the blends, the PVC was slightly stabilised, but there was a considerable destabilisation of the polycarbonate. The latter phenomenon has been explained in terms of a reduction in molecular weight in the temperature region which dehydrochlorination was occurring in due to migration of chlorine radicals from the PVC phase to the polycarbonate phase, where hydrogen abstraction from methyl groups in the polycarbonate was believed to occur.

In another study, the thermal degradation of PVC/poly(ethylene adipate) (PEAD) blends has been studied over the whole composition range, using TVA and TG [22]. In TVA studies, degradation products have been separated and characterised, and in the TG experiments both isothermal and temperature programmed conditions have been used. The blend system has been found to show very similar behaviour to the PVC/poly(tetramethylene sebacate) system previously investigated, involving some stabilisation of PVC at low to moderate PEAD

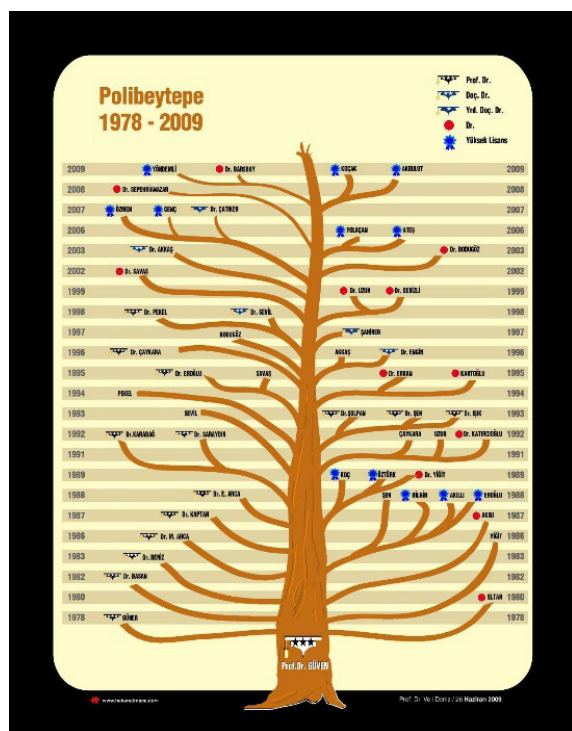


Figure 1. M. Sc. and Ph. D. students of Dr. Güven between 1978- 2009.

compositions, but destabilisation at high PEAD contents. A similar degradation mechanism in the blends was proposed, involving interaction of chlorine radicals from the PVC with PEAD, following by cross inking.

In the next study, binary blends of PVC and the maleic anhydride-allyl propionate (MA-AP) copolymer have been prepared in tetrahydrofuran solution, aimed the improvement of the thermomechanical properties [23]. The blends in the form of films have been studied using thermomechanical analyzer (TMA). The glass transition temperatures (T_g), thermal expansion coefficient (α) and other thermomechanical data for the blends have been calculated. Consequently, according to increase in ratio of the MA-AP copolymer in the mixture, the MA-AP copolymer has a plasticizing affect on the PVC.

The Preparation and Thermal Degradation of Maleic Anhydride Copolymers and Terpolymers

In the first study of this group, maleic anhydride (MA)-styrene (St)-allyl propionate (AP) terpolymer has been produced with MA, St, and AP [24]. It has been then reacted with n-propyl alcohol (Pr), n-butyl alcohol (Bu), n-pentyl alcohol (Pn), and benzyl alcohol (Bz) under certain conditions to produce ester derivatives of the terpolymer. These ester derivatives have been designated alkyl maleate terpolymers (PrMA-St-AP, BuMA-St-AP, PnMA-St-AP, and BzMA-St-AP). The polymers have been investigated by solubility and viscosity experiments, with the number of ester groups in the polymers determined by chemical analysis. They have been also characterized by Fourier transform infrared spectroscopy (FTIR), with thermomechanical properties measured via stress-strain curves.

In another study, MA-St-MMA, MA-St-VA and MA-S-AP terpolymers have been synthesized in methyl ethyl ketone from methyl methacrylate (MMA), vinyl acetate (VA), allyl propionate (AP), styrene (S), and maleic anhydride (MA) monomers according to free radical polymerization in the presence of 2, 2'-azobisisobutyronitrile

(AIBN) as initiator at 70°C for 1 hour [25]. The characterization of terpolymers has been done with the characteristic peak observed in FTIR. The viscometric analysis of terpolymer solutions has been used to obtain information about molar mass of terpolymers. For thermomechanical analysis of terpolymers, the stress-strain and penetration-temperature curves of film samples have been recorded. A change in T_g values has been observed according to MA-St-MMA < MA-St-VA < MA-St-AP series.

In the next study, firstly, the terpolymers have been produced by using monomers, MA, St and vinyl acetate taking the mole proportions of 2:1:1 in the methyl ethyl ketone in presence of AIBN as initiator at 70°C. After this, the ester derivatives of MA-St-VA terpolymer have been obtained by using propyl, butyl, pentyl and benzyl alcohols [26]. The solubilities of terpolymers and their esters were provided in tetrahydrofuran, toluen, cyclohexanone, acetone and water which have been chosen as widespread used solvents.

The unit viscosity factor and ester number of each polymer have been determined by viscometric methods. Since transformation of MA to n-alkyl maleate increases the number of ester side groups on the main chain; it can be thought that this can help the ester derivatives to dissolve easier.

Stress-strain curves of the polymers have been recorded to determine the thermomechanical characteristic of the MA and the n-alkyl maleate terpolymers. Some thermomechanical parameters such as the elasticity modulus (E), maximum stress and strain without deformation were obtained from TMA curves. Stress-strain curves apparently revealed that the terpolymer ester derivatives were more elastic than the terpolymer, because they possessing lower E values.

In this study, copolymer of maleic anhydride-hepten-1 (HPMA) has been used for preparing functional polymers since active agents can be linked to it via ring opening reaction of anhydride unit [27]. HPMA has been reacted with hexamethylene diamine (HMDA) to

obtain with amide and imide derivatives of HPMA. These derivatives have been called as maleamide-hepten-1(MAHP) and maleimide-hepten-1 (MIHP) copolymers. It has been studied the thermal behavior of these copolymers by Differential Scanning Calorimetry (DSC) and TGA. Thermogravimetric analysis indicates that MAHP-MIHP decomposed with two steps at about temperatures 125 and 325°C while HPMA began to decompose in one step at 325°C.

In the present study, first, maleic anhydride-styrene (MA-St), maleic anhydride-allyl phenyl ether (MA-APhE), maleic anhydride-heptene-1 (MA-Hp), and maleic anhydride-allyl propionate (MA-AP) copolymers have been synthesized in different solvents in the presence of AIBN at 70°C [28]. Then, these four copolymers have been reacted with aniline at 60°C in *N,N*-dimethyl formamide (DMF), and maleamic acid derivatives of these copolymers have been synthesized. Next, they have been obtained from their maleimide derivatives by heating under vacuum at 150 °C. All these polymers have been characterized by FTIR and investigated their thermal properties by using DSC and TGA methods. The analysis results showed that thermal properties of maleimide derivatives of maleic anhydride copolymers changed as depend on the neighbor monomers of MA.

In this study, the anhydride units in maleic anhydride-styrene-methyl metacrylate terpolymer (MA-St-MMA) have been reacted with *n*-propyl, *n*-butyl, *n*-pentyl and *n*-benzyl alcohols, and the ester derivatives of MA-St-MMA terpolymer have been obtained [29]. These have been named *n*-alkyl maleate ester derivatives, abbreviated as *n*PrMA-St-MMA, *n*BuMA-St-MMA, *n*PnMA-St-MMA and *n*BzMA-St-MMA. The aim of this study has been to obtain more elastic polymers by replacement with the MA units in MA-St-MMA terpolymer of alkyl groups having a linear chain structure. All the polymers synthesized have been characterized by FTIR, TMA, the solvent definition, the number of esters and solution viscosity. The TMA experiments of all the polymers have been studied at increasing temperature. All these studies have showed that the *n*-alkyl maleate ester derivatives are more

elastic than original MA-St-MMA terpolymer.

In this study, the functionality of MA has been utilized in the MA-St-MMA terpolymer [30]. First, the polyester of PEAD, PEAD, polycondensation copolymer has been synthesized from ethylene glycol and adipic acid monomers. PEAD has been then modified on its maleic anhydride units in the MA-St-MMA terpolymer which has been synthesized previously. This modified copolymer has been characterized by FTIR The viscosimetric and thermomechanical characterization of MA-St-MPAA terpolymer and its modified copolymer have been also performed and the results have been compared. The modified copolymer obtained has been found to be more elastic and more soluble, and to have lower viscosity and density.

Conclusion

The second branch in left side of polymer tree that grown by Professor Olgun Güven has produced the articles more than 30 and reading paper more than 100 on various topics of polymer and polymer technology at new established departments of chemistry and chemical engineering in Anatolian Steppe. The studied topics are the preparation and investigation of graft copolymer structures with γ -rays, the determination of gelation dose of γ -irradiated polymers, the thermal degradation of γ -irradiated polymers, the determination of thermal gelation points of polymers, comparison of various isothermogravimetric methods and new compact method and the preparation and thermal degradation of maleic anhydride copolymers and terpolymers. Some of those studies have been worked with Professor Olgun Güven in the main polymer garden in Beytepe, the others have been performed in the secondary garden in Sivas and Çorum with or without him. No matter where the branch of our polymer tree in the gardens is watered by river from the source of Professor Olgun Güven.

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