Heat Treatment of Polymers: A Review

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Abstract

Heat treatment of the polymers is considered one of the most effective methods of modification to widen their applications. Heat treatment of polymers improves their mechanical and tribological properties. This effect is a result of crystal phase increase in the polymer structure, where the elastic part of polymer viscoelasticity increases causing significant increase in compressive strength and heat conductivity. The physical and mechanical properties of polyamides are considerably affected by the degree of crystallization, which can be controlled by the change of cooling rate during the production process. Presence of small particles such as fine silica dust in polyamide matrix can alter the nucleation and cause significant increase in tensile strength and hardness accompanied by reduction in the ductility and impact strength. It is essential to consider the variation of the morphology of the cast polymer because of the difference in the cooling rate from the surface to the center, where the outer surface will be less crystalline due to the rapid solidification rate and may be less resistant to wear.

Keywords

Heat Treatment, Polymers, Mechanical and Tribological Properties

1. Introduction

Polymers heat treatment is considered one of the most effective methods of modification to widen their application. It was concluded that heat treatment of polyamide improved its tribological properties, [1]. Nowadays, much attention has been paid to fabricate a kind of absorbing materials to solve the problems of traditional microwave absorbing materials that cannot use at high temperature, low mechanical properties, heavy weight, the narrow absorption bandwidth, and so on.[1,2] Among them, polymer radar absorbing material not only can combine the properties of the polymer matrix but also can use different fillers to provide the necessary electromagnetic performances to reduce or weaken electromagnetic wave, which have attracted much interest because of their extensive applications in microwave absorption.[2–5] However, traditional polymer matrix owing to low mechanical properties and heat resistance limits them using as absorbing material matrix, so it is necessary to use a kind of high performance polymer matrix to fabricate absorbing materials. Thermosetting polyimide resin has received a great interest because of its high temperature stability, mechanical properties, and good chemical resistance, which makes it a versatile material with applications on lightweight structural materials capable of withstanding high temperature. [6–8]

This effect is a result of crystal phase increase in the polyamide structure, where the elastic part of polyamide viscoelasticity increased causing significant increase in compressive strength and heat conductivity. The influence of heat treatment of polymethyl methacrylate, (PMMA), poly tetrafluoro ethylene, (PTFE) polyamide (PA) and polyethylene terephthalate (PETP) on their friction and wear was investigated, [1, 2]. Polymeric materials were heated up to 100 °C for 12 hours then air, water and furnace cooled. Scratch and adhesive wear tests were carried out to investigate the abrasive and adhesive wear resistance,
respectively. Test results show that, friction coefficient and wear of the tested polymers were much influenced by heat treatment. For abrasive wear, as the cooling rate increased the plastic deformation of the polymer increased causing significant reduction in friction and wear, where the water cooled test specimens represented minimum wear and friction. For adhesive wear, PETP represented the minimum wear values followed by PA, PMMA and PTFE.

2. Effect of Heat Treatment on Polymers Properties

Polymers heat treatment is considered one of the most effective methods of modification to widen their application. The heat treatment of polymers can improve their mechanical and tribological properties. This effect is a result of crystal phase increase in the polymer structure, where the elastic part of polymer viscoelasticity increases causing significant increase in compressive strength and heat conductivity. Gears, bearings and other machine elements are exposed to a load spectrum consisting, amongst others, of a relative movement, causing heat and wear, and a surface pressure in an application dependent environment. This is especially true for systems without external lubrication, where melting, material fatigue and wear are the lifetime-limiting factors, [1].

The dynamic thermo-mechanical analysis technique was used to investigate the effect of pre-heat treatments on the viscoelastic properties of Ultra-High Molecular Weight Polyethylene (UHMWPE) as a function of frequency and temperature, [3]. The UHMWPE specimens were preheated at 50, 80 and 100 °C for periods of 2 and 4 h, respectively. The effect of these pre-heat treatments on the quasi-static mechanical properties (Young's modulus, yield strength, fracture strength, ductility and micro-hardness) has also been investigated. Finally, the degree of crystallinity of the UHMWPE has been measured as a function of pre-heat treatment time and temperature. The results show a strong dependence of most of these properties on the degree of crystallinity which is a function of pre-heat treatment temperature and duration.

There is an increasing demand to reduce the wear of UHMWPE. Due to such concerns, the scientific literature contains extensive information dealing with improving wear behaviour as well as the mechanical properties of UHMWPE using different techniques such as cross-linking, cold and hot drawing, and also pre-heat treatments, the subject of the present paper [4 - 15].

Hard carbon films were prepared on steel substrates by heat treatment of a polymer-poly (phenylcarbyne) at various temperatures in an Ar atmosphere. The influence of heat treatment temperature on the microstructure, surface roughness and mechanical properties of the resulting films was investigated by spectroscopy, atomic force microscopy (AFM), nanoindenter, scratch and ball-on-disk sliding tests, [16]. The preparation at 800 °C gave rise to carbon films with the maximum hardness and the hardness dropped with the higher temperature due to graphitization. In addition, with increasing heat treatment temperature, critical load of the carbon films, the ability of friction reduction and wear resistance increased gradually. The influence of the heat treatment temperature on the mechanical properties of the hard carbon films is discussed in combination with the structural analysis.

The crystallinity in deformed and heat treated semi-crystalline PET, [17 – 20], was investigated. The analysis reveals that crystallinity decreases during deformation. It was suggested that amorphization (decrystallization) is a deformation mechanism which takes place as an alternative to crystallographic slip depending on the orientation of the nanocrystalline PET lamellae. Heat treatment leads to the recrystallization of amorphous material and to an enhancement of the original orientation distribution of the crystals observed before heat treatment. This phenomenon was explained in terms of oriented nucleation where amorphous material crystallizes alongside existing crystalline lamellae.

The deformation mechanisms in semi-crystalline polymers were studied, [21 - 24]. It was found that the crystalline portions of PE, Nylon, and PET mainly deform by crystallographic shear on crystallographic chain slip planes. The weak van der Waals bonding between neighboring covalently bonded molecule chains allows for glide between such chains. Symmetry considerations show that crystallographic slip in PET does not provide five independent shear systems as required for a closed yield surface, owing to the low (triclinic) symmetry of PET crystals. This means that the von Mises compatibility criterion is violated when assuming crystallographic slip as the only mode of plastic deformation.

In the present work, the heat treated test specimens of the common used polymers such as polyethylene, (PE), polymethylmethacrylate, (PMMA), polyamide (PA), polyethylene terephthalate, (PETP) and polytetrafluoroethylene, (PTFE) on their friction and wear was investigated.

Surface structure and its correlation with conducting properties of polyaniline (PANI) ultra-thin films were studied as a function of thickness and annealing time, [25]. They are technologically interesting due to their potential as highly
tailorable semiconducting organic materials. Controlling the ordering of the film via interfacial interactions is an important step towards correlating between conductivity, and surface behavior of thin films of conducting polymers.

It was found that annealing of the granular deposits of some polymers with solvent vapor fuses a deposit into a continuous, clear film. Quantitative X-ray microscopy was used in combination with Scanning Force Microscopy to monitor the phase separation of spun cast thin films of polystyrene and poly (methyl methacrylate) blends upon annealing. Both techniques complement and enhance each other in elucidating the complicated structures that develop as a function of annealing time, [26 - 37]. Subsequently the sudden rearrangement into domains much smaller than those originally formed was observed.

X-ray reflectivity was used to measure the morphological profiles of thin gold (Au) layers of three different average thicknesses sandwiched between two polystyrene layers with different molecular weights. The morphology of samples with layers more than 4 nm thick, where a continuous layer structure was formed, were influenced by annealing, [38]. Comparison of transmission electron micrographs from unannealed and annealed samples showed that annealing promotes spherical shapes for the Au particles and breakup of an elongated, randomly connected structure visible prior to the annealing.

Polymers are often used in thin film geometries in such applications as low dielectric interlayers, insulators and adhesives of fabricated metallic structures in integrated applications, [39]. Understanding of the metal/polymer interface is also important for fundamental issues including dewetting, [40], diffusion, [41] and surface wave spectra, [42]. Numerous studies have focused on the behavior of thermally evaporated metallic particles on polymer substrates and shown that the physical properties at the metal/polymer interface are complex, [43 – 48]. The evolution of these particles can also be influenced by the presence of air/polymer interface. For example, when such systems are heated above the glass transition temperature of the polymer substrate, the assembled noble metal clusters tend to diffuse into the polymer substrate, [43, 44]. The morphological evolution of such metallized polymer composites during annealing is expected to be a function of the average metal layer thickness, or, more specifically, the average metallic particle size and interparticle spacing. Factors including particle size, effective cross-linking of polymers, and their interactions at the interface appeared to affect the properties. It was observed, [49 – 51], a very high miscibility in the blend of 43,000 MW poly (butylene terephthalate) (PBT) and 25,000 MW polycarbonate (PC) after annealing.

Thermal preconditioning has a very strong effect on the macroscopic behaviour of glassy polymers. Polyvinyl chloride (PVC) test samples were quenched and annealed. The quenched samples exhibited uniform deformation in tension while annealed samples showed necking. The temperature effect on the macroscopic behavior of glassy polymers like polystyrene (PS) and polymethylmethacrylate (PMMA) was investigated at different temperature using compression and tensile tests. It was found that temperature plays an important role on the mechanical properties of polymers. It was shown that yield stress and strain softening decrease as the temperature decreases. In tensile tests, PMMA showed a transition from brittle at elevated temperature. In contrast polystyrene was found to be brittle in the entire range of temperatures used during investigation. In a recent study of the effect of temperature on the polystyrene toughening, [52], it was found that strain softening decreases as the temperature increases. Furthermore, the transition from brittle to ductile was determined at certain level of strain softening. At a certain level of temperature PS possessed a ductile behavior.

It was observed that the microhardness of polymeric surfaces decreased as cooling rate increased, [53]. This behavior was found when the microhardness of polyamide coatings was measured to investigate the effect of the metallic reinforcement on the cooling rate during preparation. Addition of solid lubricants, metallic and nonmetallic powders to polymeric materials such as graphite, molybdenum disulphide, bronze, tin and lead powders was tested to reduce friction and wear, [54 - 59]. It was observed that favourable wear resistance was exhibited as a result of providing friction reducing materials and affecting the cooling rate of the polymers.

The physical and mechanical properties of polyamides are considerably affected by the degree of crystallization, which can be controlled by the change of cooling rate during the production process. Presence of small particles such as fine silica dust in polyamide matrix can alter the nucleation and cause significant increase in tensile strength and hardness accompanied by reduction in the ductility and impact strength. It is essential to consider the variation of the morphology of the cast polymer because of the differences in the cooling rate from the surface to the centre, where the outer surface will be less crystalline due to the rapid solidification rate and may be less resistant to wear, [60, 61].

The influence of heat treatment of polyamide (PA) and polytetrafluoroethylene (PTFE) on their friction and wear was investigated, [62]. Polyamide was heated up to 50, 80, 100 and 120 °C, but PTFE was heated up to 50, 100, 150 and 200 °C then air, water and furnace cooled. Scratch test was
carried out to investigate wear resistance and friction coefficient of the tested polymers. Test results show that, friction coefficient and wear of PA 6 were much influenced by heat treatment. As the cooling rate increased, both friction and wear decreased and the water cooled test specimens represented minimum wear and friction. Besides, no significant enhancement in friction and wear was observed for PTFE test specimens, except at 200 °C of treatment temperature, slight reduction in friction and wear was observed.

In many machine parts, which have sliding or rolling contacts, low friction and high wear resistance are demanded to increase efficiency, service life and to decrease running costs. Generally speaking, a material that has low friction usually has low wear resistance. On the other hand material that has high wear resistance has high friction coefficient. Therefore, binary coatings that have low friction coefficient and high wear resistance were developed and their tribological performance reported [63]. In this study PTFE reservoirs were arranged in such a way that the load on the contact, at any given moment, was supported by both PTFE and hard coating. Polymer–metal compounds are increasingly used, for example, in applications that cannot tolerate external lubrication such as aerospace, food industries and medical treatment products.

To produce enhanced wear resistance and also low coefficient of friction, specimens were prepared using the two different metallic coatings and three types of PTFE reservoirs. Friction and wear tests for three types of pin were carried out on a pin-on-plate arrangement under dry conditions. This new approach to enhance tribological properties of surface coatings is presented in this paper, together with the results of friction and wear mechanism studies, [64].

Friction is able to induce wear phenomena, especially for soft materials like polymers. The visible consequence is wear (weight loss), with also the possibility of a surface damage (scratch, etc.). These surface damages can alter the efficiency of the polymer layer (vision in the case of glasses for example) or generate esthetical defects (especially in the case of coatings like paint or varnish). Friction and wear mechanisms are still partly unsolved, due to the complexity of these phenomena, involving both chemical, mechanical and rheological properties and also the coupling of interfacial and bulk contributions.

The consequence of friction on nano-wear of polystyrene is analyzed and to be better understand the role of chains length in the nano-wear behavior. Studies will be focused on the analysis of the transfer layer induced by the friction of a polystyrene cylinder in contact with a hydroxylated silicon wafer, [65]. Friction experiments are performed with a translation tribometer which measures the tangential force between the polymer cylinder and the substrate for controlled normal force and friction speed. The transfer layer is analyzed using atomic force microscopy (AFM). Tentative correlations between transfer layer characteristics (roughness, shape, etc.), friction conditions (speed, normal force) and interfacial and bulk polymer properties are proposed.

Polytetrafluoroethylene (PTFE) finds an exceptional position in the plastic industry due to its outstanding chemical and heat resistance, electrical insulation and its significant low friction coefficient [66]. It is usually blended with other polymers or reinforced as a composite material for special purpose applications [67 - 69]. Both thermoplastic and elastomeric fluoropolymers find a wide use in automotive applications such as seals, O-rings and gaskets for tribological purposes [70]. Although, it has a unique low friction characteristic, it suffers from high wear rate because of its smooth molecular morphology [71]. For this reason, it is extensively used in conjunction with various kinds of fillers, thermoplastics and resins [72 - 77]. Newly developed chemically coupled PTFE compounds have opened a new way in producing enhanced wear resistant materials for high performance tribological applications [78 - 79]. A new class of potential wear resistant materials based on modified PTFE micropowder filled styrene–butadiene–styrene (SBS), acrylonitrile–butadiene–rubber (NBR) and EPDM compounds were also produced [80]. Irradiated PTFE micropowder grades were also utilized in NBR to obtain wear-resistant material for sealing applications [81].

Friction and wear could be reduced by the use of PTFE powder as a friction modifier additive in EPDM. Electron induced changes in PTFE powder significantly affects peroxide crosslinking of EPDM thereby resulting in different cross linking density of EPDM vulcanisates. Further investigations related to the influence of agglomerate size, morphology and state of cross linking on modified PTFE filled EPDM are required. These investigations are necessary because they determine final properties of compounds such as friction and wear resistance, [82].
Nowadays there exist about 20 distinct groups of commercial plastics, each with numerous grades available to obtain an optimum property profile for the corresponding application (Plastics Europe, 2007a). An overview of the commercially significant polymers along with information on their molecular structure, the internationally standardized nomenclature and abbreviations are provided in ISO 1043 (2001). On the other hand, plastics grades consist of the polymer, on the other a variety of additives is used to tailor plastics grades for specific applications. Depending on their market share and their performance properties for structural applications, i.e., the mechanical properties and the temperature resistance, plastics are divided into so-called commodity type plastics (PE, PP, PVC and PS), engineering plastics (PMMA, PC, PA, PET, PBT, POM), and specialty plastics (PSU, PES, PEI, PI, PPA, PPS, PEEK) (Plastics Europe, 2007b).

Hence, the overall objective of the research performed was to systematically investigate the aging behavior of potential plastics absorber materials and to elucidate the mechanisms of physical and chemical aging for service and application-near conditions. Part 1 of these series of two papers covers the aging behavior of four engineering plastics, while Part 2 deals with the aging behavior of four commodity type plastics (polyolefins), [83].

The computer simulation of polymer processing is an essential tool to predict the properties of the final product. For an adequate calculation, one needs to make a coupling between several physical phenomena: phase change, crystallization, thermo dependency of several parameters like the viscosity, the density, the heat capacity and the thermal conductivity. The knowledge of the rheological and thermophysical material characteristics is then of great importance. To understand the crystallization process of semi-crystalline thermoplastics, it is necessary to take into account the kinetics of crystallization and to consider the temperature and crystallization dependency of all the thermophysical properties of the material. All these variable parameters make the simulation more complicated. Generally, the simulations are simplified by considering isothermal or isobaric cases. In this work we have employed multiphysics software based on FEM method to study the coupling between heat transfer and crystallization kinetics during the solidification of a semi-crystalline polymer, such as polypropylene. First, the polymer studied was precisely characterized and the parameters of the model of crystallization are identified, using Differential Scanning Calorimetry (DSC) experiments, [84].

### 3. Effect of Heat Treatment on the Abrasion Resistance of Thermoplastic Polymers

Material properties such as the mechanical behaviour and melting-temperature significantly affect the performance of the machine elements such as gears and bearings. The mechanical and thermal properties of several semi-crystalline thermoplastics can be enhanced by radiation cross linking by changing the chemical structure of the polymer under the influence of electron beam irradiation. This cross linking mainly occurs in the amorphous regions of semi-crystalline thermoplastics. Due to the use of cooled moulds in the injection moulding process these regions are usually located near the surface, which is especially critical in tribological applications. Combined with the enhanced temperature resistance a significant extension of the operating range of thermoplastic gears is expected. Machine elements consisting of this radiation cross linked polymer can be operated at higher ambient temperature and resist higher friction loads.

![Fig. 1. Heating of the test specimens.](image1)

![Fig. 2. Cooling in water.](image2)
Ayman A. Aly, present work to investigate the effect of heat treatment on the friction and wear of polyethylene (PE), polypropylene (PP) and polystyrene (PS). Three types of the most common used polymeric materials are tested, polyethylene (PE), polypropylene (PP) and polystyrene (PS). The tested materials were in form of flat sheets \((50 \times 50 \times 4\, \text{mm})\). Test specimens were heated up to 60, 80, 100 and 120 °C for 10 hours then furnace, air, oil, water and salt water cooled, Figs. 1 – 3.

The test rig, used in the experiments was top scratching tester equipped with an indenter to produce a scratch on a flat surface with a single pass. The details of the test rig are shown in Fig. 4. The indenter, used in experiments, was a square insert \((12 \times 12\, \text{mm})\) of TiC of tip radius of 0.1 mm and hardness of 2800 kp/mm². The scratch force was measured by the deflection of load cell. The ratio of the scratch force to the normal force was considered as friction coefficient. Wear was considered as the wear scar width of the scratch. The width was measured by optical microscope with an accuracy of ± 1.0 µm. The tested surface was ground by an emery paper (500 grade) before testing. The load was applied by weights. The test speed was nearly controlled by turning the power screw feeding the insert into the scratch direction that was adjusted to be 2 mm/s. The applied load values were 10 and 20 N.

4. Conclusion

A survey has been conducted and showed that the interest in Heat treatment of polymer-based composites for technical applications, in which low friction and low wear, is increasing. The survey showed that the mechanical properties which have been improved include fatigue resistance, fracture toughness, tensile strength, wear resistance, and friction coefficient. From the results of the conducted studies there are:

- As the rate of cooling decreased hardness of the tested polymers increased and consequently friction coefficient remarkably decreased.
- Quenching test specimens in oil, water and salt water possessed relatively lower hardness with relatively higher values of friction coefficient.
- The variation of friction coefficient increased with increasing the temperature of heat treatment.
- Wear of the tested polymers decreased as the cooling rate decreased. The effect of heat treatment on wear increased with increasing temperature of heat treatment
- The change in the friction and wear properties of polymers caused by heat treatment can be attributed to the change of their crystallization.

References


