

The electrically conductive polymer with Self-healing and shape-memory features based on Polyketones/MWCNT composite through hydrogen bonding and thermoreversible Diels-Alder interactions

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ABSTRACT

An emerging type of intelligent material is the so-called shape-memory materials (SM). SM can respond to particular external stimuli by changing their shape in a dependable and reproducible way. Due to the abundance of desirable features, including chemical stability and modification, among other SM, shape-memory polymer composites (SMP) have been at the forefront of research studies. This study aimed to prepare an electrically conductive polymer nanocomposite with shape-memory (SM), and self-healing (SH) features based on furan modified polyketones (Pk-fu) and multiwall carbon nanotubes (MWCNTs). The polymer composites went through 25% of furan modifications and crosslinked by thermoreversible Diels-Alder cycloaddition between furan and maleimide moieties. For the purpose of improving properties, various formulations, including polyketones grafted with OH groups as a thermoplastic polymer, were explored. First, the physical and chemical characteristics of samples were established through characterization techniques, including ¹H-NMR, FTIR, TGA, and rheology. These characterizations proved the accuracy of modification and crosslinking. The ¹H-NMR analysis was also used to quantify the evaluation of conversion of carbonyl moieties of Pk to pyrrole groups through the modification. The rheology analysis not only supported a prosperous crosslinking, but also, it showed the disparity in the mechanical properties among different samples as the result of crosslinked density, presence of thermoplastic polymer, and adding MWCNTs. Samples with a higher amount of crosslinked density and MWCNTs showed higher storage modulus (G') at 50 °C. SM behavior was demonstrated in two different methods by applying electrical current and heat. It was determined that the samples with the additional of Pk-OH exhibited more and faster shape recovery due to the presence of hydrogen bonding. In order to evaluate the repeatability of the SM feature, samples tested for 10 deformation cycles. The result showed that the shape recovery was relatively stable for 10 cycles, and it was between 75 to 90%. Finally, qualitatively and quantitively, the SH properties were examined. The results demonstrated that the modulus of the sample drops significantly by applying the scar. However, they could recover their mechanical properties after the SH procedure. This study presented a multifunctional polymer nanocomposites with the potential to be used in functional applications such as actuators.

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1.1 INTRODUCTION

1.2 SMART MATERIALS

Smart materials are thought of as materials which have a controlled-manner response to an external stimulus to conduct a determined function [1]. However, this explanation is too general since almost all materials react somehow to a stimulus. Therefore, it is better to define smart materials as materials that respond to particular external stimuli and respond in a valuable, dependable, and reproducible way [1]. They can respond to specific or multiple stimuli such as temperature, electric or magnetic field, pH, light intensity. These stimuli induce macroscopic responses that depend on the physical and chemical properties of materials [2]. The ability to change in smart materials makes them suitable in the design of multiple intelligent applications such as tissue engineering[3], actuators[4], or medical applications[5] (for example, cardiovascular applications[6]). Moreover, polymers can be used in developing smart devices in terms of their chemical structures, architectures, and their modification ability[2]. Two fields of well-known smart materials are considered in this report which are:

- 1. Shape memory materials
- 2. Self-healing materials

1.2.1 SHAPE MEMORY MATERIALS

Shape memory (SM) materials are a class of smart materials that can return to their original shape after imposing a temporary form through the application of an external stimulus, for example, heating it [7]. Arguably, shape memory alloys (SMA) and shape memory polymers (SMP) are the most widely known SM materials [7]. In SMA, the SM ability is due to its martensitic crystal structure, which can be deformed and change to its cubic austenite crystal structure repeatedly without bond breakage. Thereafter it returns to its pre-established permanent shape [5]. Compared to SMA, SMP has the advantages of high elasticity in deformation, low price, potential biodegradability, and biocompatibility. They also have a comprehensive range of application temperatures that can be tailored and subsequently quickly processed [8]. The temperature range for SMA is only between -180°C to a maximum of 200°C depends on the type of SMA [8].

The SM effect in SMP can be graphically described by mechanical measurement under controlled stress in a mechanical analyzer [9]. The response of an SMP to a thermomechanical cycle as a 3D plot is shown in Figure 1. Applying a load at elevated temperature causes a deformation that can be fixed during cooling, as observed by the unloading curve at room temperature. Therefore, the work applied to the sample can be saved as latent strain energy if the recovery of polymer chains is restricted by crystallization or other means (Figure 1, fixing, and cooling curves). This fixed state can be stable for a long time. Upon further heating, the saved strain energy can be released as the polymer chains are reverted (Figure 1, recovery curve). The return to the original shape is arranged during crosslinking, which can be chemically or physically done. The response of a sample without a shape fixing capacity in the temperature range is also examined in the same cycle in Figure 1b (natural rubber). Noticeably, the sample returns to primary strain by unloading it at low temperatures [9].



Figure 1: 3-D plot of the schematic shape memory cycles: (a) an SMP, (b) natural rubber [10].

The SM networks rely on the presence of two kinds of network connections (reversible and irreversible) to establish a temporary and permanent shape [7]. Irreversible bonds keep the original shape. A reversible network has the ability to isolate a temporary shape in a strained state and operate shape recovery upon reheating [7]. The classical SM effect is achieved by heating beyond the glass transition (T_g) or the melting temperature (T_m) of an amorphous or a crystalline polymer, respectively. The material is deformed in its elastomeric state, and thereafter it is cooled below the transition temperature to freeze the deformation. This is shown in Figure 2 below. Subsequently, the polymer can recover to its original shape by reheating to beyond T_g/T_m [7].



Figure 2: A molecular schematic representation of the SM cycle for a semi-crystalline polymer[7]

A new generation of SMP is based on reversible binding groups (RBG), which can act as a molecular sticker that forms dynamic linkages [7]. Based on the type of RBG, the appropriate stimulus affects the rate of bond exchange and the concentration of disassociated groups. Either covalent (chemical) or noncovalent (physical) RBG can associate with SM effects in SMP, as shown in Figure 3. Noncovalent interactions are usually based on hydrogen bonding, metalligand coordination, ionic interactions, and π - π stacking. Relevant covalent chemistries are based on Diels-Alder {4 1 2} cycloaddition, transesterification and reversible addition-fragmentation reactions, photoreversible {2 1 2} cycloaddition, and disulfide bonds [7].



Figure 3: Types of SM materials based on chemical and physical bonding [7].

By using RBG, the temporary network is establishing for a triggered SMP, as is depicted in Figure 4. As illustrated in structure 1, the polymer is heated to higher than Tt (the temperature that RBG is detached), then the deformation is applied under stress (structure 2), under a subsequent cooling RBG are associated, and the temporary shape is fixed (structure 3). Reheating to above Tt cause dissociation of RBG, and the SMP can recover its primary shape [7].



Figure 4 SM cycle for an SMP bearing RBGs [7]

1.2.1.1 SMPS BASED ON HYDROGEN BONDING (NON-COVALENT RBG)

Hydrogen bonds are electrostatic interactions among a donor and an acceptor, which are known as short-range, dynamic, and directional interactions with the rate of exchange with temperature [11]. Although the strength of the hydrogen bond is relatively weak, it is many times higher than the thermal energy at room temperature. Hence, it influences the total physical properties of the material [12].

Hydrogen bond association with polymers allows the preparation of polymer networks with a thermoplastic elastomer (TPE)[13] as well as inherited SH and SM characteristics[14,15]. For instance, hydrogen bonds in telechelic and low molecular weight polymers behave as rubbery solids at low temperatures but viscous liquids at higher temperatures due to dynamic reversibility [13]. The usage of strong hydrogen bonding (for example, quadruple hydrogen bonding ureidopyrimidinone) [16] and fewer strong hydrogen bonds (for example, hexamethylene diisocyanate) [17] has been reported to prepare SMP with excellent SM behavior.

1.2.1.2 SMP BASED ON DIELS-ALDER CYCLOADDITION (COVALENT RBG)

The thermoreversible Diel-Alder (DA) bond is the most utilized reversible covalent bond, which has been used in various advanced materials such as SH structures [18,19] and reversible adhesives [20]. One of the most common examples of DA is furan-maleimide (Fu/Ma). The synthesis of which is shown in Figure 5. At below 60°C, a {4+2} cycloaddition reaction occurs between a nucleophilic diene and an electrophilic dienophile, which is driven by the formation of two stable sigma bonds and the loss of two more unstable pi bonds [21]. At elevated temperature, Fu/Ma adduct undergoes retro Diels-Alder (rDA) reaction, where at 100°C and at 135°C endo- and exo- isomers are formed respectively. This desired range leads to the popularity of DA in polymer applications [22].



Figure 5: Diels-Alder reaction between furan and maleimide groups

The DA bond presents high bond strength in comparison with non-covalent interactions. For instance, for the Fu/Ma bond, a strength of 96.2 kJ/mol has been reported, which is appreciably more substantial than an average hydrogen interaction [7].

SM characterization has been reported by utilizing biodegradable polymers in two ways. Firstly, by using PLA (polylactic acid) and PCL (poly ϵ -caprolactone) separately. Secondly, with the blending with other polymers as a polymer backbone and Fu/Ma Diels-Alder as a thermoreversible bond, which is shown in Figure 6[23–29]. Fast self-healing (SH) and tunable SM features with responses to different stimuli have been reported for these materials. Moreover, thermoreversible recyclable polymers based on polyketones and DA have been studied [19,30–35]. It is reported that with a low degree of DA crosslinking, SM features were observed. Whereas at the high degree of crosslinking did not show these features [33].



Figure 6: Schematic illustration of SM and SH of PCL/polyurethane containing Fa/Ma DA units[36].

1.2.2 SELF-HEALING MATERIALS

Self-healing (SH) materials are a type of smart material with the ability of automatic or autonomous healing, similar to SH behavior observed in various living organisms [37]. Inspired by natural materials, investigation in synthetic SH materials focused on the production of multifunctional materials that can recover their primary properties after damage, including mechanical properties, electrical conductivity, and corrosion resistance [38]. The SH ability in materials exhibits an increased lifetime and new potential applications [37].

Among various materials, polymer nanocomposites are leading candidates in numerous applications due to their superior properties such as strength, low cost, stiffness, lightweight, and thermal stability [39]. Nevertheless, these materials also suffer from shortcomings such as surface scratches and degradations [37]. The involvement of SH into polymer nanocomposites offer a new way toward sustainable materials for multifunctional applications [37]. SH polymer nanocomposites are expected to have the combined benefit of nanoparticle inclusion without cracking, which plagues traditional nanocomposite polymers [37].

1.2.2.1 SELF-HEALING PROPERTIES OF POLYMER NANOCOMPOSITES

Polymer-based materials have wide applications due to their characteristics, such as high flexibility, lightweight, easy processing [37]. However, in comparison with other materials such as metals and ceramics, the majority of polymers show lower modulus and strength [40]. The physical and mechanical properties of polymers can be improved by the incorporation of nanomaterials [41]. The combination of polymer and nanoscale materials results in the development of a unique material with interesting properties. However, the formation of cracks/ micro-cracks can occur in polymer nanocomposites during synthesizing, transport, and handling. Therefore, the final features, including mechanical properties, are usually more muted than expected. To overcome this problem study of SH properties of polymer and nanoparticles can be healed in polymer nanocomposite, as shown in Figure 7 [37].



Figure 7: Scheme of polymer nanocomposite with the SH ability of micro cracks

Nanomaterials based on carbon, including carbon nanotubes and graphene, have been gaining interest in applications of SH properties in polymer nanocomposites [37]. The main advantages of these nanomaterials are high surface/volume ratio and fascinating thermal, electrical, optical, and mechanical properties. Due to carbon-based nanoparticle surface characteristics, they interact with the polymer matrix through covalent and non-covalent interactions, including van der Waals forces, hydrogen bonding, and π - π stacking [37].

1.2.3 CARBON NANOTUBE COMPOSITES WITH SH AND SM PROPERTIES

The discovery of carbon nanotubes (CNTs) opens a new field of interest within nanotechnology in 1991 [42]. CNTs are rolled graphite sheets of a hexagonal pattern of carbon atoms with a nano-range diameter. Two forms of CNTs exist, single-wall carbon nanotubes (SWCNT) (manufactured by a single layer of carbon) and multi-wall carbon nanotubes (MWCNT), which consists of layers of coaxial carbon rolled sheets as shown in Figure 8 [43].



Figure 8: Structure of carbon nanotubes [44]

At first academic research about CNT/ polymer nanocomposites was mostly on SWCNTs because of their more straightforward structure compared to MWCNTs [43]. However, due to the reasonable cost and industry-scale production of MWCNT, the research interest has been changed to MWCNT polymer nanocomposites [43].

SM polymers and CNT have been used to prepare foams with SH properties[45]. Li *et al.* (2008) used SM polystyrene, MWCNT, and glass micro-balloons followed the fabrication of composite plates with a foam core by vacuum-assisted resin infusion molding technology. Healing efficiency was characterized at room temperature after different impact damage by scanning electron microscopy (SEM). Their study indicated that the presence of CNT enhances the strength and the SM recovery rate of the material.

In another study, Sinha-Ray *et al.* (2012) prepared SH nanocomposite by an encapsulation technique [46]. SH liquid monomers (dicyclopentadiene and isophorone diisocyanate) and CNT were encapsulated inside polyacrylonitrile polymer fibers by using electrospinning, coelectrospinning, and emulsion solution blowing. After squeezing the fibers in between two copper plates, the healing agents are released through the broken fiber cross-section or broken fiber shell. Then the healing occurs by a polymerized healing agent in the presence of their corresponding catalysts. The intercalation of carbon nanotubes and healing agents also offer a self-sustained diffusion method.

Another study used a crosslinked hybrid that is fabricated from furan-modified poly(styrenebutadiene-styrene) (SBS-Fu) and CNTs via Diels-Alder reaction [47]. This hybrid demonstrates smart behaviors, including SM and SH, via DA and rDA reactions. Moreover, the CNTs play an active role in energy transfer through the media. Intellectual properties are triggered by both thermal stimulus and laser irradiation.

In previous works by the Picchioni research group, rapid SH features have been demonstrated with nanocomposites based on polyketone, carbon nanotubes, and Diels-Alder crosslinks [31,32,48]. It was found that a moderate amount of carbon nanotubes (5%) can elevate electrical conductivity and intrinsic SH. Consequently, the electrical, mechanical, and thermal characteristics of the polymer network remain the same after damage followed with healing [48].

1.2.4 POLYKETONES

Figure 9 shows aliphatic polyketones with ketones groups in their backbones as one class of polymers with promising chemical and physical properties with a high potential to prepare functional polymers by chemical modification [49]. First aliphatic polyketones were synthesized in 1941 by the random copolymerization of carbon monoxide and ethylene in extreme conditions (230°C, 2000 bar) [50]. Ethene/CO copolymer (ECO) is a semi-crystalline thermoplastic with a crystallinity range between 35-50 wt% [50]. However, ECO polymers are unstable just above their melting point temperature (around 268°C) [51]. In 1980, the highly efficient synthesis of aliphatic polyketones based on palladium catalyst and mild conditions (90°C, 40-50 bar) was reported [52]. The latter method is used to synthesize (ethylene-propene-CO copolymers) EPCO, which has a lower melting point; therefore, the limitations for polymer processing decrease. This discovery attracted considerable interest, which has continued until today in using polyketones in both academia and industry[51].



Figure 9: The scheme of the dimer structure of polyketones

Based on the reaction conditions and metal catalyst design, the properties of EPCO can vary from highly amorphous elastomers to highly crystalline thermoplastics [53]. During polymerization, if the ethene/propene molar ratio is less than 0.5, the final EPCO exhibits typical properties of amorphous polymers which have a low molecular weight, while above this molar ratio, the EPCO is a crystalline thermoplastic [53]. The crystallinity provides the gas barrier properties against water vapors and oxygen for polyketones, which with biocompatible properties, make them potential polymers for food packaging [51,54]. Besides these good properties of high molecular weight thermoplastic polyketones, the presence of carbonyl groups is the main feature for these polymers, which provide them the ability of post-modification [51]. Indeed, highly polarized carbonyl groups (C=O) can display high reactivity

(nucleophilic addition) [55]. During the modification, the C=O groups can convert to thiols, alcohols, cyanohydrin, methylene, and oximes functional groups, as shown in Figure 10 [51].



Figure 10: Carbonyl and dicarbonyl chemical modification [51].

Polyketones can also be modified during the eco-friendly Paal-Knorr reaction without any solvent and catalyst under relatively mild experimental conditions [51].

1.2.4.1 PAAL-KNORR REACTION

The 1,4-dicarbonyl groups present in EPCO terpolymers have shown exceptional reactivity toward alcohol, thiol, or amines [51]. This reaction, which occurs through multiple steps, is known as the Paal-Knorr reaction, as shown in Figure 11 [56].



Figure 11: The Scheme of Paal-Knorr Pyrrole reaction steps of EPCO

R' can vary from at least a methylene unit to any functional groups based on the final application [51]. The Paal-Knorr reaction is carried out in mild conditions (110°C, 1 atm) without any catalyst and solvent [52]. The hardness of the polymer backbone increases as a result of aromatic groups that can be controlled during modification. The hardness on polymer even adds value for purpose applications [51].

1.2.5 INDUSTRIAL RELEVANCE OF SMP

During the last few decades, the activities in chemical industries have been changing from common chemicals to specialty chemicals and products such as personal and household products, functional polymers, and biomedical devices[52].

A branch of polymer engineering is developing smart functionalities, for instance, possible widespread application for smart polymers in technical devices [8]. To conclude the previous parts, a real trend in polymer science is a design of multifunctional material with different methods such as blending, compositing, modification, and crosslinking to have a combination of functionalities such as conductivity, SH, SM, and recyclability. An important concept to design this multifunctional material is polymer systems. In a polymer system, final product properties (for example, SM) can be various by only a change in chemical composition. Therefore, the final product, as an SM material, can be used in different applications such as actuators, orthodontic wires, medical cast, expandable extends, and packaging [57].

2 OBJECTIVE

This work aims to design an intelligent material that presents SM and SH properties upon applying heat and electric current. In order to achieve this, a conductive composite based on carbon nanotubes and furan-crafted polyketones crosslinked with bismaleimide will be explored. An example of this is shown in Figure 12. Polyketones have been chosen as they are easy to use and have eco-friendly properties. For the purpose of improving properties, various formulations, including polyketones grafted with hydroxyl groups, will be explored.



Figure 12: Polymer composite based on carbon nanotubes, polyketones based on Fu/Ma

3 EXPERIMENTAL

3.1 MATERIALS

Polyketones (Pk30) (synthesized according to previous works [51,52], the EPCO terpolymers with 70% of propylene, and 30% of ethylene and molecular weight (MW) of 2687 Da, shown in Figure 13. Other materials used in the research are listed in Table I.

Material name	Chemical formula	Purity	Properties	supplier
Furfurylamine (Fu)	NH ₂	≥99 %	MW=97.02 gr/mol density=1.05 gr/ml	Sigma Aldrich
3-amino-2-propanol (OH)	H ₃ C NH ₂ OH	≥99 %	MW=75.11 gr/mol density=0.982 gr/ml	Sigma Aldrich
Butylamine (Bu)	NH ₂ H ₃ C CH ₃	≥99 %	MW=73.13 gr/mol density= 0.74 gr/ml	Sigma Aldrich
Multiwall carbon nanotubes (MWCNT)	Carbon	95 %	The average length of 5 μm and O.D. of 6-9 nm	Sigma Aldrich
1,1-(methylenedi-4,1- phenylene)bis- maleimide (Ma)			MW=358.35 gr/mol	Sigma Aldrich
Chloroform	CHCl ₃	99.5 %		Sigma Aldrich
Deuterated chloroform	CDCl ₃	99.8 atom% D		Sigma Aldrich

Table I: The materials used throughout the research



Figure 13:A scheme of a dimer of Pk30 (R₁=H 30%, R₂=CH₃ 70%)

3.2 METHODS

3.2.1 POLYKETONE FUNCTIONALIZATION (PAAL-KNORR REACTION)

The functionalization of polyketone was carried out through the Paal-Knorr reaction in bulk state without the presence of any solvent. For weighting the Pk30, a heat gun was used to warm up the polymer and pouring in the round-bottomed glass reactor. The reactor set with a U-type anchor impeller and reflux condenser in an oil bath. Pk30 was preheated at 110°C with a stirring speed of 600 rpm. The functionalizing agent (furfurylamine, butylamine, or 3-amino-1-propanol, as shown in Figure 14) was added dropwise with a rate of 0.2 ml/min. Then the reaction continued for 4 h. The torque of the stirrer was changed from 3.5 N at the beginning of the reaction to 7 N at the end, as the functionalization makes the polymer harder. The resulting functionalized Pk30 was cooled down to room temperature. 100 ml of chloroform solvent was added, and the mixture was left for 24 h in order to dissolve the polymer and facilitate the polymer extraction from the reactor. The resulting solution was washed with 500 ml of Milli-Q water in separation glassware three times to remove leftover amine groups. The final product was poured in a Teflon plate and kept inside the fume hood to evaporate the majority of the solvent. Additionally, the vacuum oven was used at 70°C for 48 h to remove the solvent.



Figure 14: Paal-Knorr reaction of modification of polyketones by a) butylamine, b) 3-amino-1-propanol, an c) furfurylamines

The molar ratio between the polyketones and the functional groups was established with a maximum conversion of 25% to the carbonyl. According to Table II, the Pk30 is modified chemically by furfurylamine, butylamine, and 3-amino-1-propanol (Fu, Bu, OH).

Table II: Polyketones samples with chemical modifications

sample	Pk30 (gr)	FU (gr)	BA (gr)	AP (gr)	Total (gr)
Pk30-FU25%	30	5.53	-	-	35.53
Pk30-Bu25%	30	-	4.16	-	34.16
Pk30-OH25%	30	-	-	4.28	34.28

3.2.2 POLYMER CROSSLINKING

The Diels-Alder reaction provides three-dimensional and reversible crosslinking network structures. Bismaleimide was used as a crosslinking agent, and the multi-walled carbon nanotubes (MWCNTs) were used as the reinforced material. The final samples should not dissolve in the chloroform solvent. For preparing samples, first, MWCNTs were dispersed in chloroform solvent (0.5 vol.%) in a sonication bath for 30 minutes. Functionalized polymers based on the composition which are needed for the final sample were dissolved in chloroform (10 vol.%) in a round-bottom flask with a reflux condenser attached. Then the solution of

functional polymers was mixed, and the suspension of MWCNTs was added to the solution and stirred at 50°C for 2h using an oil bath equipped with a temperature controller. Bismaleimide with the ratio of 2:1 (furfurylamine (Fu): bismaleimide (Ma)) at equimolar amounts was added, and the blend was continuing stirring at 50 °C for 24 h, as is shown in Figure 15. The final product was poured in a Teflon plate and keep inside the fume hood to evaporate the majority of solvent followed by the drying in a vacuum oven at 80°C for 24h. Furthermore, the samples were ground into a fine powder and were further dried in the vacuum oven at 60°C for another 24h.



Figure 15: preparing polymer nanocomposite with DA reaction

Crosslinked polymer nanocomposites with different formulation are prepared as they are listed in Table III. For naming the samples, the abbreviation of components is used. Table IV is used to explain the naming convention used for one example. Table III: the composition of polymer nanocomposites samples

Samples	Pk30-Fu25 (gr)	Pk30-OH25 (gr)	PK30 (gr)	PK-Bu25 (gr)	MWCNT (gr)	Ma (gr)	Total (gr)
Pk-Fu	5	-	-	-	-	0.85	5.85
Pk-FuCNT-5%	5	-	-	-	0.308	0.85	6.158
Pk-Fu:Pk30 (9:1)	5	-	0.55	-	-	0.85	6.4
Pk-Fu:Pk30 (9:1)-CNT5%	5	-	0.55	-	0.336	0.85	6.736
Pk-Fu:Pk30 (8:2)	5	-	1.25	-	-	0.85	7.1
Pk-Fu:Pk30 (8:2)-CNT5%	5	-	1.25	-	0.373	0.85	7.473
Pk-Fu:OH(9:1)	5	0.55	-	-	-	0.85	6.4
Pk-Fu:OH (9:1)CNT5%	5	0.55	-	-	0.336	0.85	6.736
Pk-Fu:OH(8:2)	5	1.25	-	-	-	0.85	7.1
Pk-Fu:OH(8:2)-CNT5%	5	1.25	-	-	0.373	0.85	7.473
Pk-Fu-CNT8%	5	-	-	-	0.493	0.85	6.343
Pk-Fu:OH(8:2)-CNT8%	5	1.25	-	-	0.597	0.85	7.697
Pk-Fu:Bu(8:2)-CNT8%	5	-	-	1.25	0.597	0.85	7.697

Table IV: the naming convention used for all samples

Abbreviation	Definition
Pk	polyketones with 30% of ethylene and 70 % of propylene
Fu	Pk30 is modified by furfurylamine with 25 %,
OH	Pk30 is modified by 2amino-1propanol with 25 %
Bu	Pk30 is modified by butylamine with 25 %
(8:2)	the ratio of mixing Pk30-Fu25 to Pk30-OH25 is 8 to 2
CNT8%	carbon nanotubes were added with the 8% wt.

3.2.3 SAMPLE PREPARATION WITH MOLDS

Three stainless steel molds are used to prepare samples for further tests. The first mold had 8 rectangular holes with dimensions of 35 mm x 6 mm x 1 mm was used for bar preparation for conductivity tests. The second mold had 8 U-shape holes, as shown in Figure 16 are used for SM tests. The last mold had 25 disc-shaped holes with a diameter of 8mm, and a thickness of

1.2 mm was used for SH and rheometric tests. Molds are properly cleaned with sandpaper and acetone and covered by PTFE spray. Holes are entirely filled with ground powder of dried materials, then both sides of the mold lined by Teflon paper and pressed by Hotpress TP400 Fontune Holland machine under 40 bar pressure at 150 °C for 30 minutes.



Figure 16 U-Shape sample dimensions

3.2.4 CHARACTERIZATION

3.2.4.1 ELEMENTAL ANALYSIS

Elemental analysis was used to evaluate the conversion of carbonyl moieties of Pk30 to pyrrole groups by calculating the nitrogen of the final product according to Equation 1 [51].

Equation 1: the formula used for calculating the conversion of carbonyl group [51].

$$X_{CO} = \frac{\left[\frac{N \times 0.01}{14 \times n}\right] \times PK30(gr)}{\frac{PK30(g)}{M_{PK}} - \frac{PK30(gr)}{M_{PK}} \times M_{Amine} \times \left[\frac{N \times 0.01}{14 \times n}\right] + 2 \times \frac{PK30(gr)}{M_{PK}} \times M_{water} \times \left[\frac{N \times 0.01}{14 \times n}\right]}$$

Where:

 X_{CO} = conversion of carbonyl groupsN= nitrogen percentage in the final product
(determined by elemental analysis) M_{PK} = average molar mass of each unit of
product M_{water} = molecular weight of watern= number of nitrogen atoms in each unit of
product M_{Amine} = molecular weight of amine
compound

The conversion efficiency η is also defined as Equation 2:

Equation 2: conversion efficiency of the conversion of carbonyl group [30]:

$$\eta = \frac{X_{co}}{X_{co}^{feed}} \times 100\%$$

The X_{co}^{feed} is calculated as Equation 3

Equation 3: the amount of carbonyl group that was calculated from the amount of adding amine

$$X_{co}^{feed} = \frac{Mol_{amine}}{Mol_{d-CO}} \times 100\%$$

Where:

 Mol_{amine} = the moles of amine compounds Mol_{d-CO} = the moles of di-carbonyl units in the feed.

3.2.4.2 PROTON NUCLEAR MAGNETIC RESONANCE (¹H-NMR)

The ¹H-NMR measurement was done by NMR Oxford AS400 for evaluating the succus of chemical modification of polyketones. Samples were prepared by dissolving in CDCL₃ solvent (4% vol). After complete dissolving, the solutions were transferred to ¹H-NMR vials. The assignment of the peaks is performed using the NMRPredict Desktop software Mestrenova. 64 scans were done for the 400 MHz measurements to have maximum sensitivity.

3.2.4.3 FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Thin film or powder of samples was used to analyze samples by IRtracer-100 Shimadzu to evaluate the success of modification and crosslink of samples. Before each measurement, the background scan was done. The measurement is recorded at the range between 4000 cm⁻¹ and 500 cm⁻¹ with a resolution of 4 cm^{-1,} and the final spectra are the average of over 64 scans. Final spectrums were normalized to a comparison between samples got possible.

3.2.4.4 THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA was performed by Thermogravimetric Analyzer TGA4000 PerkinElmer to measure the sample degradation temperature and residual after burning. A small amount of each sample (around 2 mg) put in TGA ceramic cups and they are heated from 50°C to 850°C with a rate of 10° C/min under N₂ atmosphere.

3.2.4.5 CONDUCTIVITY TEST

Electrical parameters were measured for both bar and U-shape samples, as shown in Figure 17. The silver paste was applied on both end sides of the samples, which connected to the copper clamps, then covered by aluminum foil and put under the clamps of the holder.





The length between the clamps was fixed and was the same for different samples. Therefore, by applying a determined voltage (V), and measuring current (I), the electrical resistance (R) was calculated as Equation 4.

Equation 4: The formula used for calculating electrical resistance.

$$R = V/I$$

The units which are used for resistance, voltage, and current are ohm (Ω) , volt (V), and ampere (A), respectively.

The electrical resistivity (ρ) is known as a parameter that shows the resistance of a material and is calculated as Equation 5.

Equation 5: the formula used for calculating electrical resistivity.

$$\rho = R A/l$$

Where

R= electrical resistance (Ω)

A = cross-sectional area (m²)

l= the length between two clamps (m)

The electrical conductivity (σ) which represents the ability of materials to conduct electricity was also calculated as

Equation 6: The formula used for calculating electrical conductivity.

$$\sigma = 1/\rho$$

The units for the electrical resistivity and electrical conductivity are ohm-meter (Ω .m) and siemens per meter (S/m), respectively.

3.2.4.6 MECHANICAL PROPERTIES BY RHEOMETER TESTING

The mechanical properties of cross-linked samples were analyzed by Hybrid Rheometer Discovery HR-2 as a function of temperature using the discovery Hr-2 model rheometer. The geometry of parallel plates with an 8mm diameter was used. The amplitude sweep test was conducted with the range of strain from 10⁻³ % to 10% at a controlled axial force of 8 N and a frequency of 1 Hz. Storage and loss moduli were measured as a function of different oscillation strain at two fixed temperature (50°C and 120°C). Moreover, the temperature ramp mode covering temperature from 50 to 120 °C was performed, and storage modulus, loss modulus, and tan delta as a function of temperature are determined.

3.2.4.7 SHAPE MEMORY PERFORMANCE OF SMPS

Shape recovery is an essential parameter in SM behavior. For evaluating SM function, mechanical bending procedure [58] and rheometer testing were used. After thermal treatment of samples at 50 °C for 24 h, The mechanical bending procedure includes the following steps (illustrated in Figure 18): (step 1) U-Shape samples were heated up by applying electricity to around 120 °C and were bent to storage angle 90° and/or 45°; (step 2) samples were cooled by compressed air to freeze the deformation; (step 3) the current was applied again (at 30 and 40 V) and an SMP recover to an angle (recovery angle). The shape recovery time (the time between states 2 and 3) was recorded for 10 times for each sample. This method was used to quantify the SM performance.



Figure 18: SM performance, step1: original Shape, step2: bending state, and step 3: recovered Shape

Another method was used to quantify SM behavior by using Discovery Hr-2 Rheometer. The SM behavior was quantified in terms of shape recovery ($X_{recovery}$) and recovery rate ($V_{recovery}$) for disc-shaped samples with 8 mm diameters geometry. To do so, first, the sample was heated up, and the deformation was applied under 8 N. The sample was then cooled to about ambient temperature without releasing the strain to freeze the temporary shape. Subsequently, reheating to initial temperature resulted in an apparent recovery.

Equation 7:Shape recovery rate

$$V_{recovery} = \frac{S_R - S_I}{t_R}$$
 (rad/S)

Equation 8: Shape recovery quantity

$$X_{recovery} = \frac{S_I - S_R}{S_I} \times 100 \qquad (\%)$$

Where S_I and S_R represent the initial strain before unloading and strain after recovery, respectively. t_R also designates the duration in seconds that shape recovery takes.

4 RESULTS AND DISCUSSIONS

4.1 POLYKETONES CHEMICAL MODIFICATION

The functionalization of polyketones was performed by the reaction of PKk30 with furfurylamine, 3-amino-1-propanol, and butylamine in bulk state. The reaction proceeds to conversion of carbonyl groups (with 25% modification) in 4 hours [30,31,51,52]. The samples after modification have a brownish waxy appearance with high viscosity at room temperature. ¹H-NMR measurement before and after modification of Pk is shown in Figure 19. Results presented the proof of polyketones modification. In the spectra of Pk-30-Fu25 broad peaks at 5.98, 6.25 and 7.3 are assigned to the hydrogen atoms of pyrrole rings[51,52]. In the spectra of OH-grafted polyketones (Pk30-OH25) (Figure 19c), peaks at 1.05 ppm and 1.96 ppm related to methyl groups on the polymer backbone and pyrrole ring respectively. The peak at 3.8 ppm indicates the proton from the CH groups located between the methyl and hydroxyl groups [30]. In a similar way, the spectra of Pk30-Bu25 (Figure 19d) displays the proton peak related to the methylene group at 1.35 and the proton signal at 0.93 associated with the methyl group for the Bu moiety [59].

In order to determine the experimental amount of conversion of carbonyl groups (X_{CO}), two procedures were used. First, X_{CO} was calculated by ¹H-NMR spectra results. From the ratio of peaks at 1.05 ppm (methyl moieties on the polymer backbone) and at 1.96 (methyl moieties from the pyrrole ring), it is also possible to determine the experimental amount of conversion of carbonyl groups (Figure 19b)[14,52]. Second, the elemental analysis method was used as it was described earlier in part 3.2. Because of the high viscosity of Pk30-OH25 and Pk30-Bu25 samples, the elemental analysis only was possible for the Pk30-Fu25 sample. The outline of the results is displayed in Table V.



Figure 19: ¹*H-NMR spectra Pk30 a) before and after modification with Fu and model compound reaction of Pk with b) Fu, c)OH, and d)Bu*

	Elemental analys	sis results	¹ H-NMR results		
Samples	X _{CO} (%)	η(%)	X _{CO} (%)	$\eta(\%)$	
Pk30-Fu25	22.4	89.4	14-18	56-72	
Pk30-OH25	-	-	10-15	40-60	
Pk30-Bu25	-	-	21-25	84-100	

Table V: The experimental amount of carbonyl group conversion and conversion efficiency.

The difference between elemental analysis results and ¹H-NMR results for the Pk30-Fu25 sample as well as low conversion efficiency that ¹H-NMR results show, indicate the accuracy for calculating conversion from ¹H-NMR results were not sufficient enough.

FT-IR spectroscopy was used to confirm polyketones modifications, and results are shown in Figure 20. The IR technique is widely used to study changes on polymer surface after modification. However, because of the sampling thickness for the IR method, this method is often insensitive. The thickness of the sample is usually considerably more significant than the modified layer thickness. Therefore, the intensity of functionalities might be very low [60]. The spectrum for the Pk30-Bu25 sample is shown in Figure 20a. Based on literature reports [60,61], as the result of modification with Bu, a small broad peak between 3200 cm⁻¹ and 3600 cm⁻¹ corresponding to stretching vibration of N-H bonds in a secondary amine should be formed. The intensity of this peak is relatively low in the Pk30-Bu25 sample of this work. However, the intensity for this peak in the literature was relatively low as well.

As it is shown in the Figure 20a, polyketones modified with 3-amino-1-propanol (Pk30-OH25) has a broad peak between 3400 and 3500 cm⁻¹ and a sharp peak at 840 cm⁻¹ which associated to hydroxyl stretch groups in the polymer backbone of the product as it was shown previously in Figure 14b [30]. In the IR spectrum of Pk30-OH25, there is no evidence for a possible reaction between carbonyl and hydroxyl groups. Figure 20b shows the spectra of Pk30-Fu25. The peaks at 1440 cm⁻¹ and 1385 cm⁻¹ are related to furan and pyrrole ring stretching in the polymer backbone of Pk30-Fu25, as it was shown previously in Figure 14c. Furthermore, 1013 cm⁻¹ and 1073 cm⁻¹ peaks refer to furan and pyrrole C=C stretching [51,62].



Figure 20: FT-IR spectra of modified polyketones modified with a) Bu, b) OH, and c) Fu

The functionalized polyketones were also analyzed by TGA, which determined their thermal stability, which is shown in Figure 21. Both modified polymers remained stable up to around 400 °C. Therefore, they are suitable for the processing required to create nanocomposites. Above 100°C, the small weight loss (1-2%) was recorded, which is attributed to the solvent evaporation. Pk-Fu sample displayed the highest thermal stability, perhaps due to the radical scavenging features of the pyrrole rings [32].



Figure 21 TGA results for chemical modification of polyketones

4.2 PREPARATION OF POLYMER NANOCOMPOSITE THROUGH DIELS-ALDER REACTION

Thermoset-thermoplastic blends are materials with a mixture of desirable properties of both thermoplastic and thermoset polymers [63]. By adding thermoplastic polymer to thermosets, samples become more rubbery, and their brittleness decreases. However, the main problem in Thermoset-thermoplastic blends is the phase separation that occurs because of the difference in their chemistry [64]. This work intends to introduce improved materials by combining thermoset and thermoplastic polymers to overcome the brittleness of modified polyketones samples as it was reported as a problem in previous works [30,31]. To do so, Pk30-Fu25 was mixed withPk30-OH25 and Pk30 before crosslinking. The Pk30-Bu25 was also added to
Pk30-Fu25 thermoset as a control experiment to evaluate the role of OH groups in the thermoplastic. Face separation was not expected and observed since both polymeric components have the same polymer backbone, i.e., polyketones.

Crosslinking of samples through the DA reaction was carried out at 50 °C for 24 h in the presence of bismaleimide (Ma). All samples were prepared with and without MWCNT to investigate the effect of MWCNT. Chloroform was used as a solvent to dissolve reactants and disperse MWCNT. According to previous works, FT-IR analysis has been performed to analyze the DA cycloaddition reaction[30,31,51,52]. Figure 22 illustrates the FT-IR results for all samples before and after crosslinking. The C-O-C ether peak (1182 cm⁻¹) of reacted furan [51,52], appears after crosslinking. Furthermore, a new peak also arose at 1378 cm⁻¹, related to the C-N stretching of maleimide rings, which supports the bismaleimide presence [51].

Although the result of the presence of 3-amino-1-propanol, the absorptance of OH groups in 3500 cm⁻¹, should be found in the spectra of samples containing OH, this peak did not appear. This could happen due to the low percentage of OH-containing compounds when hydrogen bonding is prevented through a lack of molecular contact [65].



Figure 22 FT-IR spectra of cross-linked polyketones nanocomposites

4.3 THERMAL PROPERTIES OF CROSS-LINKED POLYMER NANOCOMPOSITES

Thermal gravimetric analysis (TGA) was performed to evaluate the material thermal properties. In this research, the TGA was carried out under an inert gas (nitrogen) at a temperature range of 50 to 850 °C, and with a heating rate of 10 K/min. In the interest of saving space, some results are shown in this part, and the rest are in Appendix1.



Figure 23: TGA results for polymer nanocomposite with 80% of Pk30-Fu25 and 20% of thermoplastic polymers.

As the TGA results are illustrated in Figure 23, all samples decomposed at around 400 °C as the main backbone of the polymer, which was the major component of the samples, degraded. The degradation temperature for Pk nanocomposites with MWCNTs was lower than their composites without MWCNTs, probably due to aggregation of MWCNTs, which has been reported by Lim et al. (2015) [66].

In general, samples with higher degradation temperatures have more char after degradation [67]. In this case, Pk showed a higher degradation temperature than its composites, but its char yield was unexpectedly lower than the composites. This indicates that cross-linking and the presence of MWCNTs improved char-forming capacity. However, MWCNTs did not have decomposition fully until 850°C and form abundant char [68]. Moreover, samples which

included MWCNTs had higher char yield compared to samples without MWCNTs. The TGA results were used to approximate the probative weight of nanoparticles in the samples, as it is listed in Table VI. 600°C was used as a reference temperature for calculation, as it was reported in Redondo-Gomez et al. (2017) work that MWCNTs were still stable at 600°C [68].

As it is shown in Table VI, there was a noticeable difference between the amount of MWCNTs added to the feed and the measured amount from TGA data. This difference might be because of the incomplete homogeneous distribution of MWCNTs [67].

samples	MWCNT supplied (%)	TGA data (%)
PK-FU-CNT5%	5	7.43
PK-FU-OH(9:1)	5	5.82
PK-FU-PK(9:1)	5	4.75
PK-FU-PK(8:2)	5	8.60
PK-FU-OH(8:2)	5	6.21

Table VI: Weight percentage of MWCNTs in polymer nanocomposites in the feed and measured by TGA

The temperature framework of this research (will be explained in further parts) was between 50 to 140 °C.; therefore, the stability of nanocomposites at this temperature range was necessary. As it is exhibited in Figure 24, there was no significant thermal degradation for all samples (less than 2% degradation). Based on Gandini et al. (2013) work [69], a degradation peak in the TGA graph should be displayed around 150 °C, equal to the crosslinking density as the result of rDA reaction (as it was determined in a TGA graph in previous work Lima et al. (2019) [70]). However, this degradation was not evident in the TGA results because of the low percentage of crosslinking in preparing these samples, as shown in Figure 23. However, another theory could explain this degradation peak at around 150 °C and might be related to the residual solvent in the polymer after drying samples. Evaporating solvent from polymer solution had a diffusion control, where the solvent must first diffuse out of the bulk of the polymer matrix to the polymer surface and then evaporate [71]. As the longer drying time and lower crosslinking densities were used in this work compared to previous work done by Lima et al. (2019) [70], this decomposition peak did not appear for these samples.



Figure 24: TGA results in the investigation temperature frame-work.

4.4 ELECTRICAL PROPERTIES OF COMPOSITES

Samples, including MWCNTs, were characterized for electrically conductivity properties. The electrical properties were determined in bar and U-Shape samples. Samples were placed between two copper clamps and the current applied through the samples. In order to improve the contact between the contact surface of samples and copper clamps, silver paste and aluminum paste are used in the surface contact of samples and clamps. The use of silver paste and aluminum confirms that the entire cross-section of samples was contacted, not only the surface. First, the conductivity of samples for bar geometry was tested. The dimensions for all bars were the same; therefore, with the voltage control power supply and measuring the current (with a multimeter), the conductivity of samples could be calculated with Equation 4, Equation 5, and Equation 6, which were previously described. The conductivity of samples and the temperature that they reached were important features that affect SH and SM properties, which will be explained in further parts.

The amount of MWCNTs 5 wt% was chosen for bars, as it was reported as an adequate amount [72,73]. As it is shown in Figure 25, the conductivity test was applied for bars containing MWCNTs. The sample without thermoplastic polymer (Pk-Fu) showed the highest conductivity as it had higher Fu attachment. This result was anticipated since it has been reported by Hermosilla and Picchioni (2016) that Fu attached to MWCNTs and got crosslinked. The overall distribution of the filler was better along with the sample, which resulted in better conductivity[48].



Figure 25: conductivity results for bar-shaped samples with 5% of MWCNTs.

The conductivity for samples with 5 wt% MWCNTs was extremely low in U-Shape geometry. As the length for U-Shape geometry was about 3 times higher than bar geometry; hence, according to Equation 5, conductivity decreased. Due to this reduction in conductivity and the maximum temperature reached was 40 °C, which was not suitable for SH and SM features. Therefore, the MWCNT content was increased for the U-shape samples to 8 wt% MWCNTs. The conductivity and temperature curves are shown in Figure 26.



Figure 26: a) Temperature and b) Conductivity for samples with 8% MWCNT with respect to voltage

Three samples were prepared with 8 wt% MWCNT in U-Shape geometry. Pk-Fu-CNT8%, Pk-Fu:OH(8:2)-CNT8% and Pk-Fu:Bu(8:2)-CNT8%. Pk-Fu-CNT8% sample was more conductive than Pk-Fu:OH(8:2)-CNT8% because of the higher crosslink density and, therefore, higher interaction between MWCNTs and Fu groups, which explained earlier. However, the conductivity of Pk-Fu:Bu(8:2)-CNT8% was the highest among other samples, which can be related to its lower T_g [32]. As the annealing was applied for all three samples at 50 °C for 24 hours, the sample with lower T_g could be annealed better [32].

4.5 MECHANICAL PROPERTIES

The mechanical properties of samples were investigated by using the Discovery HR-2 rheometer. The variation in storage modulus (G' or E'' ability of storing energy), loss modulus (G'' or E'', ability of dissipating energy), and tan δ (the ratio of loss modulus to storage modulus) as the respect to temperature (°C) and oscillation strain (γ) were measured for all samples. First, the G' and G'' were measured as the respect of oscillation strain (γ) in minimum and maximum temperature (50 and 120°C) to find the ratio of strain that the G' and G'' were in linear state and were independent to magnitude of strain as it is shown in Figure 27. Then, both moduli and tan δ were measured with respect to the temperature between 50°C and 120°C and in the strain between 0.1% and 0.2 %. All experiments were done in duplicate to consider the repeatability of samples. In the interest of simplicity, some results are shown in this part, and the rest are in Appendix 1.



Figure 27: Amplitude sweep for Pk-Fu-CNT5%

The amount and type of functionalities, presence of MWCNTs, and the ratio of polymers in a blend affect ultimate features in products. As it is shown in Figure 28, for all samples, both storage and loss moduli increased by temperature reduction. In elevated temperature (higher than transition temperature), both moduli decrease because of less force, which was needed for viscoelastic behavior and relative changes in them [74]. The maximum of tan δ is between 50 to 70 °C which is the transition temperature from rubbery to viscous state. Compared to previous work done by Lima et al. (2019) [70], the maximum of tan δ was at a lower temperature for this research which was due to the lower percentage of modification and crosslinking (25 % furan modification) explained by a lower concentration of both furan and pyrrole along the polyketone backbone which made them more flexible [33].



Figure 28: The mechanical properties for polymer nanocomposites

The presence of thermoplastic polymers affected the mechanical properties of the thermoreversible thermoset composite. As Figure 29 illustrates, an unexpected increment was present in the G' of Pk-Fu:OH(8:2)-CNT5% sample. Although the percentage of the crosslink density in Pk-Fu-CNT5% was higher, this increase might be a consequence of a synergetic effect of hydrogen bonds at reduced temperature (below 70 °C). Moreover,

Pk-Fu:Pk(8:2)-CNT5% sample had lower total crosslink density compared to Pk-Fu-CNT5%, accordingly, lower G' was obtained as it is shown in Figure 28.



Figure 29: The effect of thermoplastic polymer on the mechanical properties of polymer nanocomposite.

Reinforcing polymer with MWCNT results in increasing both moduli by orders of magnitude and lower height of $\tan \delta$ peak, as shown in Figure 30. This can be explained firstly by increasing the toughness of composite as a result of adding MWCNTs. Secondly, the strong interfacial interaction of the polymer backbone with MWCNTs reinforces. Thirdly, it has been reported that furan and maleimide groups also undergo DA reaction with CNT surface [20,31,48].



Figure 30: Mechanical properties for sample Pk-Fu including 0%, 5%, and 8% of MWCNTs

In samples with 8% of MWCNT, the mechanical properties were also investigated between 50 and 140°C, as it is illustrated in Figure 31. The G' for Pk-Fu-CNT8% was the highest because it had numerous crosslinks. In addition, with a similar trend, Pk-Fu:**OH**(8:2)-CNT8% had a more significant G' than Pk-Fu:**Bu**(8:2)-CNT8% due to hydrogen bonding.



Figure 31: Mechanical properties for polymer nanocomposite including 8% of MWCNTs

4.6 SHAPE-MEMORY PROPERTIES

For shape-memory behavior in SMP, the RGB should partially detach to isolate the temporary shape, as is shown in the scheme in Figure 32.

Qualitatively and quantitively, SM behavior was demonstrated in two different methods. In the first method, after thermal treatment of samples at 50 °C for 24 h, U-Shape samples were heated up by applying electricity to around 120 °C and were bent to 90° and/or 45°. Then, by cooling down the samples, the temporary shape was fixed at room temperature. Finally, an electrical current was applied again (at 30 and 40 V), and the temperature was raised to a maximum of 120°C to recover the original state (shown previously in Figure 18). The shape recovery time (the time between states 2 and 3 in Figure 18) was recorded for 10 times for each sample. This method was used to quantify the SM performance.



Figure 32: a scheme of SM behavior in an SMP with RGB

order to evaluate the outcome of the SMP formulation, PkFu-CNT8%, In PkFu:OH(8:2)-CNT8%, and PkFu:Bu(8:2)-CNT8% samples were tested. Figure 33 shows the shape velocity rate for all three samples as a function of bending angle (Θ) and voltage (v). It shows that the Pk-Fu-CNT8% sample had the fastest recovery compared to other samples. This can be explained by the crosslinked density of samples as Pk-Fu-CNT8% had the highest degree of crosslinking (other samples had 80% of Pk-Fu, which can be reacted by bis-Maleimide and get crosslinked). Clearly, more bonds can participate in DA and rDA reaction to freeze a temporary shape and recover the original shape. The Pk-Fu:Bu(8:2)-CNT8% sample was the most conductive sample, and it was able to reach higher temperatures among other samples, shown previously in Figure 26. As well, compared to samples, both PkFu:OH(8:2)-CNT8% and PkFu:Bu(8:2)-CNT8% samples had the same crosslinked density. Thus, lower recovery time was quite surprising for PkFu:Bu(8:2)-CNT8% sample. The faster recovery rate for PkFu:OH(8:2)-CNT8% sample can also be related to the hydrogen bonding. Hydrogen bonding can help DA reaction to fix the temporary shape and recover the original shape as it was explained in the introduction section [7].

The SM recovery time was characterized at two different bending angles. Results indicated that the recovery time for the bending angle of 90° was higher than 45° . However, the difference is not significant, which means the recovery from 90° to 45° is faster than recovery from 45° to 0° .

In order to investigate the effect of voltage in shape recovery velocity, the shape recovery time was tested in two different voltages, as shown in Figure 33. At higher voltage (40 V), the recovery was faster, which can be related to the higher temperature that samples reach at a

higher voltage (as shown previously in Figure 26). At higher temperatures, the mobility of polymer chains is higher, and SMP chains backbones can move and recover the shape faster[58]. In addition, at elevated temperature, the required energy for rDA happening could be achieved faster and allowed covalent bonding exchange [75]. Additionally, at voltage 30V, the recovery was not complete, and the final angle was about 10° (not 0°)(as shown previously in Figure 18). This occurrence can also be related to temperature. As it is shown in Figure 26, the temperature that samples reach was approximately between 50 to 60 °C. Clearly the rDA was not happening at this temperature, and the SM effect can be related to the semi-crystalline structure of Pk [7] that was explained in SHAPE MEMORY MATERIALS in the introduction section.



Figure 33: Shape recovery time of U-Shape samples as a function of bending angle and voltage

Another method was used to quantify SM behavior with more accuracy by using Discovery Hr-2 Rheometer. The SM behavior was quantified in terms of shape recovery and recovery rate for Pk-Fu-CNT8%, Pk-Fu:OH(8:2)-CNT8%, and Pk-Fu:Bu(8:2)-CNT8% disc-shaped samples with 8 mm diameters geometry. To do so, first, the sample was heated up, and the deformation was applied under 8 N. The sample was then cooled to about ambient temperature without releasing the strain to freeze the temporary shape. Subsequently, reheating to initial temperature resulted in an apparent recovery in the strain Figure 34.



Figure 34: The combined elasticity and plasticity cycle for SMP that was testing by the rheometer.

The effect of different parameters, including the initial temperature, sample formulation, strain of deformation (%), amount of shape recovery, and rate of shape recovery, was investigated. Figure 35 shows the shape recovery of the three samples for 2% of strain and at 140°C.



Figure 35: Shape recovery for three SMP with 8% of MWCNTs

As the data is listed in Table VII the shape recovery rate ($V_{recovery}$) and the quantity of shape recovery ($X_{recovery}$) (calculated from Equation 7and Equation 8 respectively) were diverse between samples.

samples	V _{recovery} (rad/s)	X _{recovery} (%)
PkFu-CNT8%	0.013	79
PkFu:OH(8:2)-CNT8%	0.014	89
PkFu:Bu(8:2)-CNT8%	0.010	62

Table VII: shape recovery and shape recovery velocity for three SMP including 8% MWCNTs

Pk-Fu:**OH**(8:2)-CNT8% sample had the most $V_{recovery}$ and $X_{recovery}$ values. As it was explained for the first method, PkFu-CNT8% had the highest crosslinked density and was expected to have the fastest shape recovery as it was in the first SM test. Nevertheless, here it seems that the hydrogen bonding in Pk-Fu:**OH**(8:2)-CNT8% sample assisted in the retention of the temporary shape; therefore, it recovered faster.

As this is shown in Figure 36, the shape recovery velocity was changed during heating up the samples during recovery. As Figure 36 presents, all three samples demonstrated faster recovery rates after around 120°C, which can be related to rDA. When the DA crosslinking detaches, the sample can recover the initial shape faster [7,75,76]. Pk-Fu-CNT8% had the highest crosslink density and the most considerable change in recovery rate as it was excepted. There was a peak in the derivative plot around 50°C that can be associated with the softening point of the samples [7,9]. Besides, for the Pk:Fu:OH(8:2)-CNT8% sample showed an additional peak located around 70 °C that clearly can be related to the breakdown of hydrogen bonding.



Figure 36: the derivative for Shape recovery for three SMP with 8% of MWCNTs

 $X_{recovery}$ was also tested at different temperature for Pk-Fu:OH(8:2)-CNT8% sample to prove the assertion that shape recovery can occur in different temperatures due to three different mechanisms: (1) DA and rDA above 100°C, (2) hydrogen bonding around 70°C, and (3) the softening point of samples around 50°C [7,9,57,77]). As it is shown in Figure 37.



Figure 37: Shape recovery (%) for Pk-Fu:OH(8:2)-CNT8% sample at different temperatures.

In order to consider the effect of deformation strain, the PkFu:OH(8:2)-CNT8% sample was also tested in different strain from 1% to 5% at 140°C as it is illustrated in Figure 38. This

period of oscillation strain was chosen because G' and G" were $\$ in their linear state between 1 and 5%. For 1 and 2% of strain the $X_{recovery}$ was more than 90%, and after 3% of strain $X_{recovery}$ drops significantly. This means by increasing the deformation strain, the ability of shape recovery decreases. However, the slip of samples in high strain deformation might be another reason that makes an error in measurement.



Figure 38:Shape recovery (%) for Pk-Fu:OH(8:2)-CNT8% sample at different strains.

In order to evaluate the degradation of the polymer and the reversibility of DA cycloaddition, $X_{recovery}$ corresponding to the number of deformation cycles (10 cycles) at an original strain of 2% at 140°C is shown in Figure 39. It shows that the recovery is relatively stable for 10 cycles, and it was between 75 to 90%.



Figure 39: The shape-memory recovery for Pk-Fu:OH(8:2)-CNT8% sample for 10 cycles.

In addition to various SM tests that have been examined for samples, the ability to erase the SM of PkFu:OH(8:2)-CNT8% sample, and applying a new shape was also tested by two procedures. In the first procedure, erasing shape history was tested by applying heat. The bar-shaped sample was heated up to 120°C and bent. This bending deformation was fixed by placing the sample in glassware vial Figure 40a. Then it was transferred to an oven at 120°C for 2 h. As it is shown in Figure 40b, the new shape was fixed, and the sample can recover it after temporary deformation (are shown in Figure 40c and d). During this procedure, rDA occurs to all crosslinked linkages (at 120°C) [51,78]. After cooling, DA bonding can fix this new shape permanently, and new shape was fixed in SMP.



Figure 40: a) Triggering a new shape in PkFu:OH(8:2)-CNT8% sample by applying heat. b) fixing a new permanent shape after 2h. c) Applying a new temporary shape. d) recovering from initialing shape

In the second procedure, the U-Shape sample was fixed between two copper clamps, and the current was applied. When the sample temperature was reached to 120°C, the sample was bent and fixed in that state for 2 h, as it is shown in Figure 41. Similar to the first procedure, a new permanent shape was stabilized. It was concluded that with both heat and electricity, adjusting the new permanent shape is possible.



Figure 41: a) Triggering a new shape in PkFu:OH(8:2)-CNT8% sample by applying an electric current. b) fixing a new permanent shape after 2h. c) Applying a new temporary shape. d) recovering from initialing shape

4.7 SELF-HEALING PROPERTIES OF SMPS

In order to demonstrate the SH features of SMP, three scenarios, as described below, were pursued.

- 1) Qualitatively SH testing by remolding
- 2) Quantitively SH testing with Rheometer
- 3) Surface SH testing by using electricity and SEM pictures

The SH properties were tested for Pk-Fu:OH(8:2)-CNT8% sample. Due to the rDA reaction in Fu-Ma bonds above 100 °C, the ability of self-repairing of cracks with a heating stimulus in SMP was supposed to occur [30,51,78].

4.7.1 SH testing by remolding

In this method, the SH featured indicated by placing the broken SMP samples back in their previously used corresponding casts, as it is shown in Figure 42. For this procedure, samples were healed by remolding in the initial process condition (at 150°C and 40 bars for 30 minutes). Although the samples were entirely healed in the bulk state, scratches on the surface of the samples were clearly visible on the breaking points, as it is shown in Figure 42c. The remaining of these scratches on the surface can be associated with not enough crosslinking density to heal the material thoroughly, as already mentioned in Lima et al. (2019) [31]. The sample with less amount of DA crosslinking had lower SH properties. In addition, some material loss in breaking points can be responsible for the incomplete healing on the surface of the samples [79,80].



Figure 42: A U-shaped of Pk-Fu:OH(8:2)-CNT8% sample: a) after molding, b) after breaking, c) after healing

4.7.2 SH testing with Rheometer

One of the most critical issues on the subject of SH and recyclable materials is no loss in properties, including mechanical properties. The recovery of properties is an essential matter in reusing the SH materials. In order to test the SH effect on mechanical properties, the Discovery HR-2 rheometer was used. First, a disc-shaped sample was tested for mechanical properties, as previously described in chapter2 (Figure 43a). The sample was then partly cut with a sharp blade, and the mechanical properties were tested for the sample with cracks between 40 and 80 °C (Figure 43b). The temperature should not be more than 80°C, as healing during the test was not required. Then, the sample was healed in the rheometer by applying a 10N axial force at 120 °C for 30 minutes (Figure 43c). Mechanical properties were tested once more after healing, and the result is shown in Figure 44. By cutting the sample, the G' decline significantly and again recovered to the initial amount after healing.



Figure 43: A disc of Pk-Fu:OH(8:2)-CNT8% sample: a) after molding, b) after breaking, c) after healing



Figure 44: G' graph for a disc of Pk-Fu:OH(8:2)-CNT8% sample, before the scar, with the scar, and after healing

4.7.3 Surface SH testing with electrical current

In order to demonstrate the surface self-healing, a bar-Shape sample was set once more in the same condition used to assess the conductivity. Several scratches were added on the surface by a sharp blade. The electrical current was applied to perform the healing as a result of triggered resistive heating. For that reason, the current was applied for 24 h while the sample reached 120 °C. The scanning electron microscopy was used to investigate the healing before and after Figure 45. unfortunately, the sample did not show surface-repairing features because of possible material loss from scratching areas and/or insufficient crosslink density as it was described previously.



Figure 45: The SEM images of the surface of Pk-Fu:OH(8:2)-CNT8% sample a) before and b) after healing with an electric current.

5 CONCLUSION

The above study aimed to investigate and analyze an electrically conductive polymer nanocomposite which showed shape-memory and self-healing features. For this purpose, polyketones 30 (Pk30) with 70% of propylene, and 30% of ethylene was used. First, to introduce different pendant groups into the polymer, polyketones were modified through Paal-Knorr reaction using furfurylamine, butylamine, and 3-amino-1-propanol. These three modifications were successfully confirmed by ¹H-NMR, elemental analysis, and FTIR. The nanocomposites were then prepared by solution mixing of different compositions of modified polyketones and MWCNTs by using chloroform as the solvent. Samples went through Diels-Alder thermoreversible crosslinking by using maleimide as the crosslinking agent. The effective crosslinking confirmed by FTIR and TGA analysis.

Samples with 5 %wt of MWCNTS showed electrical conductivity for bar-shaped samples. However, this amount of MWCNTs was not enough to trigger conductivity in U-shaped samples as their length was about three times longer than bar-shaped samples. Therefore, samples with 8 %wt of MWCNTs were prepared. They showed desirable electrical and thermal conductivity at different voltages. They also could reach elevated temperature morethan160 °C.

Rheological analysis was used to determine the mechanical properties, shape-memory (SM), and self-healing (SH) features. The amount and type of functionalities, presence of MWCNTs, and the ratio of polymers in a blend affect ultimate features in products. The sample without thermoplastic polymers showed a higher modulus due to higher crosslinked density. Moreover, higher amounts of MWCNTs lead to high modulus.

Three mechanisms were assumed to represent the SM effect in samples: 1) Diels-Alder and retroDiels-alder cycloaddition, 2) hydrogen bonding as the result of the presence of hydroxyl groups, and 3) the semi-crystalline structure of Pk30. The sample with the 20% of adding OH modified polyketones (Pk-OH), and 80% of modified polyketones (Pf-Fu), and 8 %wt of MWCNTs showed the highest and fastest shape recovery in shape-memory evaluation. It was hypothesized that the hydrogen bonding helped to fix the temporary shape and recovered the primary shape. The results showed the repeatability of shape recovery over 10 cycles. The ability to erase the shape memory of samples and imposing new shape was also achieved by both heat and electricity.

The self-healing (SH) ability of samples was investigated quantitively by testing the recovery of mechanical properties. The modulus of the sample decreases notably as the result of a scar. After healing, the sample can recover about 90% of its initial modulus. SH was also investigated qualitatively by normal pictures and SEM images. Although the perfect bulk SH was observed, the sample did not show surface-repairing features because of possible material loss from scratched areas.

The prepared smart polymer nanocomposite in this work has the potential to be used in functional applications that require electrical conductivity, and both SM and SH features such as actuators and biomedical applications.

6 FUTURE RESEARCH RECOMMENDATIONS

There are some recommendations that can be suggested for future research:

- 1. As one of the mechanisms for shape-memory effect in samples was the semi-crystalline structure of polyketones, the use of Pk50 instead of Pk30 might show more shape recovery ability.
- 2. As the polyketones are a biocompatible polymer, the prepared product in this work could be modified (for example, hydrophilic treatment) to be used in specific biomedical applications.
- 3. The replacement or the combination of MWCNT with other nanoparticles, such as reduced graphene oxide, which has hydroxyl groups on their surface, could improve shape memory behavior.
- 4. The quantification of self-healing can be improved by controlling the applied scar with different techniques.

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8 APPENDIX 1



Figure 46 TGA graphs for sample with 10% of thermoplastic Pk



Figure 47: TGA results for all samples



Figure 48: TGA graphs for samples with different amount of thermoplastic Pk



Figure 49: TGA result before and after crosslinking



Pk-Fu:Bu(8:2)-CNT8% amplitude sweep

Time t (s)

-1.0

30]




























Pk-Fu:OH(8:2)-CNT8% Amplitude sweep



































Pk-Fu-CNT8% Amplitude sweep















Pk-Fu:Pk(9:1) Amplitude sweep















Pk-Fu:Pk(8:2)-CNT5% Amplitude sweep







Oscillation strain $\widehat{\gamma}$ (%)

10-2

10-1

100

101

102

10-4

10-5

10-3







Pk-Fu:OH(8:2) Amplitude sweep









