

Photostabilization, Adhesion Strength and Solubility Evaluation of Novel Acrylic Acid Based Copolymers

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Abstract: The synthesis of novel copolymer acrylicacid-Co-N-(substitutedphenyl-1,3,4thiadiazole acryl methylamine copolymer into three steps was achieved by the reaction benzoic acid derivatives with thiosemicarbazide presence of phosphorous oxychloride(pocl3) to from compound 2-Amino-5-(substitutedphenyl)-1,3,4-thiadiazole. The purified products were reacted with allyll chloride to from compounds 2-N-(allyl amino)-5-(substituted phenyl)-1,3,4-thiadiazole). Finally the copolymers were synthesized by the free radical of compounds (B1-B5) with acrylic acid by using AIBN as initiator. All the prepared compounds (A₁-A₅), and (B₁-B₅) have been characterized based on(FT-IR), and (p₁-p₅,) based on (FT-IR, ¹HNMR, GPC, TGA,) techniques. The polymers were used as additives to PVC in calculated percentages and composites were irradiated with UV light for 300h and found to be good Photostabilization. The adhesion strength for the polymers were evaluated by using single-lapshear method. The Solubility of the polymers where ested against some solvents the polymers were soluble in some of them.

Keywords: 1,3,4-Thiadiazole, acrylic acid, copolymers, Adhesion, Photostabilization, solubility

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I. INTRODUCTION

A copolymer is a polymer derived from more than one species of monomer. The polymerization of monomers into copolymers is called copolymerization. Copolymers obtained by copolymerization of two monomer species are sometimes called bipolymers. Those obtained from three and four monomers are called terpolymers and quaterpolymers, respectively[1]; [2]. Commercial copolymers include acrylonitrile butadiene styrene (ABS), styrene/butadiene co-polymer (SBR), nitrile rubber, styrene-acrylonitrile, styrene-isoprene-styrene (SIS) and ethylene-vinyl acetate, all formed by chain-growth polymerization. Another production mechanism is step-growth polymerization, used to produce the nylon-12/6/66 copolymer [3] of nylon 12, nylon 6 and nylon 66. Is a synthetic high-molecular weight polymer of

acrylic acid .They may be homopolymers of acrylic acid, or copolymer with an allyl chloride of thiadiazole. PAA is an anionic polymer, i.e. many of the side chains of PAA will lose their protons and acquire a negative charge. This makes PAAs polyelectrolytes, with the ability to absorb and retain water and swell to many times their original volume. Dry PAAs are sold as white, fluffy powders that are frequently used as gels in cosmetic and personal care products. Their role in cosmetics is to suspend solid in liquids, prevent emulsions from separating and control the consistency in flow of cosmetics[4]; [5]. For many applications PAAs are used in form of alkali metal or ammonium salts, e.g. sodium polyacrylate. In the dry powder form, the positively charged sodium ions are bound to the polyacrylate, however in aqueous solutions the sodium ions can dissociate. Instead of an organized polymer

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chain, this leads to a swollen gel that can absorb a high amount of water. Polyacrylic acid is a weak anionic polyelectrolyte, whose degree of ionisation is dependent on solution pH [6]. Photostabilization of Poly(Vinyl Chloride) to UV-Light to avoid UV degradation in the plastic, use stabilizers or stabilizers for this purpose. For many outdoor applications, the simple addition of carbon black to the polymeric chain at a level of about 2%, the structure will be protected by the blocking process Pigments such as (TiO2) can also be compounds Effective organics such as benzotriazole and benzophenones are typical UV absorbers that can selectively absorb UV rays and reappear at a less harmful wavelength mainly as heat, the benzotriazole type is inferior and can be used at low dose rates as little as0.5%. The other main mechanism of protection is the addition of stabilizers to maintain the polymer's strength, elasticity, and toughness and protect the polymer's original molecular structure. The most common fixative is HALS (inhibitory amine light stabilizer) which can absorb the excited groups and prevent the chemical reaction of the radicals^[7]. An adhesive is a material applied to surfaces to permanently join them by a bonding process. It is a substance capable of forming bonds to each of the two or more part interfaces comprising the final object [8]. The resultant adhesion from the application of the interatomic adhesive on substrate surfaces is At the interface, and intermolecular interaction [9]. Due to a competitive pricing, polymer adhesive is widely accepted and applied worldwide. The automobile and aerospace industries have used polymers in an adhesive system found in the automotive industry: the attachment of a paint coating to a polymer bumper bar. In Polymeric stuff, also from the civil/building industry As a rubber sealant, it plays a significant function. A nice one Usage of polymer adhesives in biomedical applications Polymer glue arms to repair and fix the market will be During surgery to restore human bones[10]. Although the study of adhesion mechanisms can be traced back to the 1930s, the adhesion mechanism of polymers until today is still under debate[11]. Water-soluble macromolecules are a diverse class of polymers, ranging from Biopolymers that mediate life processes of enormous commercial utility to synthetic polymers. Polymers that are water-soluble have been classified into the biopolymer, non-ionic, ionic and associative groups, based on main structure. It is possible to transform water-soluble polymers into insoluble ones, By setting a crosslink point. Connecting while The chains of polymers that lead to polymer resins[12]; [13].

II. EXPERIMENTAL AND METHODS

The synthesis of the copolymers (P_1-P_5) are shown in the scheme below. The F.T-IR spectral data recorded on FT-IR-8400 Fourier Transform Infrared Spectrophotometer shimadzu using potassium bromide disc.1H-NMR were recorded on Bruker Ultra Shield, 500MHz, using DMSO. GPC (gel permeation chromatography) were measured Agilent GPC-Addon rev. A.02.02. TGA (Thermal Gravimetric Analysis) were recorded Rheometricscintific 1000. Chemical names follow the IUPAC nomenclature. Starting materials were used without purification.

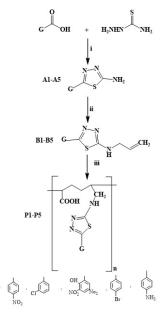


Fig. 1. POCl₃, reflux 3 h, H₂O, reflux 4 h, KOH. Allyl chloride, triethyl amine, DMF, stirring 2h,80°C Acrylic acid, benzene, AIBN, reflux 12 h, methanol

A. Synthesis of 2-Amino-5-(substituted phenyl) -1,3,4-thiadiazole (A₁-A₅)

Phosphorous oxychloride (POCl3) 0.01 mol was added drop-wise to a mixture of (0.91g, 0.01 mol) thiosemicarbazide and (0.01 mol) of an appropriate carboxylic acid under stirring. The mixture was refluxed for 3 h. Water 50 ml was added with stirring and the reflux was continued for additional 4 h. After cooling, the mixture was neutralized with 10% Potassium Hydroxide solution, filtered, washed with water and recrystallized from ethanol [14]; [15].

2-Amino-5-(4-nitrophenyl)-1,3,4-thiadiazole (A_1) Pale broun powder, yield (80%), m.p 244-246 °C; F.T-IR (KBr disk, cm-1) 3105-3294, 3053, 1612, 1600. 2-Amino-5-(3-chlorophenyl)-1,3,4-thiadiazole (A_2) Pale yellow powder, yield (81%), m.p 210-212 °C; F.T-IR (KBr disk, cm-1) 3290-3124, 3062, 1624, 1573. 2-Amino-5-(4-bromophenyl)-1,3,4-thiadiazole (A_3) Yellow powder, yield (91%), m.p 220-222°C; F.T-IR (KBr disk, cm-1) 3336-3273, 3082, 1633, 1600..

2-Amino-5-(4-aminophenyl)-1,3,4-

thiadiazole (A₅) Light yellow powder, yield (84%), m.p 220-222°C; F.T-IR (KBr disk, cm⁻¹) 3409, 3380, 3047, 1627, 1566.

2-Amino-5-(2-hydroxy-3,5-dinitrophenyl)-1,3,4 -thiadiazole (A₅) Reddish orange powder, yield (96%), m.p Above 347°C; F.T-IR (KBr disk, cm-1) 3205-3263, 3066, 1635, 1600.

2- N-(allyl amino)- 5-(substituted phenyl)-1,3,4 -thiadiazole) (B_1 - B_5). Compounds (A1-A5) (0.01mole) were dissolved in DMF (30 ml), Allyl chloride was added slowly with stirring, triethyl amine few drops were added and the mixture stirred at (80°C) for (2h). After cooling water (30ml) was added and the precipitate was filtered, washed with water and re-crystallized from ethanol [16].

2- N-(allyl amino)- 5-(4- nitro phenyl)-1,3,4 -thiadiazole) (B₁) dark yellow powder, yield (91%), m.p 210-212°C; F.T-IR (KBr disk, cm-1) 3327, 3100, 2945-2870,1660.

2- N-(allyl amino)- 5-(3-chlorophenyl)-1,3,4 -thiadiazole) (B₂) Light yellow powder, yield (90%), m.p 153-155°C; F.T-IR (KBr disk, cm-1) 3290, 3086, 2978-2910,1654.

2- N-(allyl amino)- 5-(4-bromophenyl)-1,3,4 -thiadiazole) (B₃) Light yellow powder, yield (91%), m.p 160-162°C; F.T-IR (KBr disk, cm⁻¹) 3280, 3100, 2970-2905,1674.

2- N-(allyl amino)- 5-(4-aminophenyl)-1,3,4

-thiadiazole) (B₄) Dark yellow powder, yield (75%), m.p 222-224°C; F.T-IR (KBr disk, cm-1) 3156, 3032, 2951-2890,1653.

2- N-(allyl amino)-5-(2-hydroxy-3,5-dinitrophenyl) -1,3,4-thiadiazole) (B5) Dark orange powder, yield (80%), m.p 300-302°C; F.T-IR (KBr disk, cm-1) 3280, 3039, 2958-2905,1660.

Acrylic acid-Co-N-(substitutedphenyl

-1,3,4 thiadiazole) acryl methylamine copolymer $(\mathbf{P}_1 - \mathbf{P}_5)$

A solution of compounds (B_1-B_5) (0.01mole) and acrylic acid (0.01 mole, 0.72 g) were dissolved in benzene (30ml) and was degased and purged with nitrogen gas. AIBN (0.008 mole, 1.3 g) was added and the mixture was refluxed for (12h) after cooling, methanol (30ml) was added [17] and the precipitate of the polymer was formed and hardened on time.

Acrylic acid-Co-N-(4-nitrophenyl-1,3,4 thiadiazole) acryl methylamine copolymer (P₁) Dark yellow, yield (77%), F.T-IR (KBr disk, cm⁻¹) 3277, 1732, 3172, 1631, 3088, 2978. ¹H-NMR (DMSO- d₆, 500 MHz, δ) 12.4 (s, 1H), 1.2 (t, 1H), 7.4-8.4 (m, 4H), 5.5(s,1H), 2.5(q,2H), 1.4 (m,1H), 4.2(d,2H).

Acrylic acid-Co-N-(3-chlorophenyl -1,3,4 thiadiazole) acryl methylamine copolymer (P_2) Light yellow, yield (79%),F.T-IR (KBr disk, cm⁻¹) 3423, 1735, 3178, 1614, 3066, 2997. ¹H-NMR (DMSO-d₆, 500 MHz, δ) 9.5 (s, 1H), 1.8 (t, 1H), 7.4-7.8 (m, 4H), 5.3(s,1H), 1.79(q,2H), 2.6(m,1H), 4.3(d,2H).

Acrylic acid-Co-N-(4-bromophenyl -1,3,4thiadiazole) acryl methylamine copolymer (P₃) Light yellow, yield (73%),F.T-IR (KBr disk, cm⁻¹) 3423, 1735, 3282, 1641, 3091, 2945. ¹H-NMR (DMSO- d₆, 500 MHz, δ) 11.1 (s, 1H),1.5(t, 1H), 7.1-8.1 (m, 4H), 5.02(s,1H), 1.65(q,2H), 2.45(m,1H), 4.2(d,2H).

Acrylic acid-Co-N-(4-aminophenyl -1,3,4thiadiazole) acryl methylamine copolymer (P_4) Dark yellow, yield (70%),F.T-IR (KBr disk, cm⁻¹) 3498, 1737, 3140, 1622, 3037, 2985. ¹H-NMR (DMSO- d₆, 500 MHz, δ) 10.06 (s, 1H), 1.4 (t, 1H), 7.8-8.1 (m, 4H), 6.3(s,2H), 5.9(s,1H), 1.7(q,2H),2.5 (m,1H), 4.25(d,2H).

Acrylic acid-Co-N-(2-hydroxy-3,5-dinitrophenyl-1,3,4 thiadiazole) acryl methylamine copolymer (P_5) Dark orange, yield (68%),F.T-IR (KBr disk, cm⁻¹) 3163, 1728, 3169, 1627, 3078, 2914. 1H-NMR (DMSO- d₆, 500 MHz, δ 11.2 (s, 1H),1.7 (t, 1H), 7.1-7.8 (m, 2H), 6.3(s,1H), 6.9(s,1H), 1.71(q,2H), 2.6(m,1H),4.2(d,2H).

B. Gel Permeation Chromatography analysis (GPC)

Gel permeation chromatography (GPC) is a type of size exclusion chromatography (SEC), that separates analytes on the basis of size. Polymers can be characterized by a variety of definitions for molecular weight including the number average molecular weight (Mn), the weight average molecular weight (Mw) and the size average molecular weight (Mz). Table (1) shows the factors calculated using GPC technique. The smaller analytes can enter the pores more easily and therefore spend more time in these pores, increasing their retention time. These smaller molecules spend more time in the column and therefore will elute last. Conversely, larger analytes spend little if any time in the pores and are eluted quickly. GPC is often used to determine the relative molecular weight of polymer samples as well as the distribution of molecular weights. The experimental design is not much different from other techniques of liquid chromatography. Samples are dissolved in an appropriate solvent, in the case of GPC these tend to be organic solvents and after filtering the solution it is injected onto a column. The separation of multi-component mixture takes place in the column. The constant supply of fresh eluent to the column is accomplished by the use of a pump. Since most analytes are not visible to the naked eye a detector is needed. Often multiple detectors are used to gain additional information about the polymer sample. The availability of a detector makes the fractionation convenient and accurate [18]; [19]. Figures (1) to (5) show the GPC chromatogram for the synthesized polymers with conditions 1 g/L, injected volume 20 μ L, temperature 25°C, rate of flow 1 ml/min.

TABLE 1 GPC ACTUAL FACTORS OF POLYMERS (P1-P5).

Polymer No.	Mw (g/mol)	Mn (g/mol)	Mz (g/mol)
P1	60640	121	12420
P2	63674	178	12040
P3	68403	128	13902
P4	61230	144	12800
P5	72884	125	12974

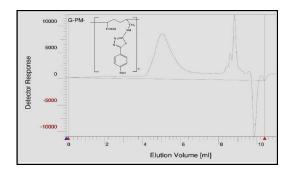
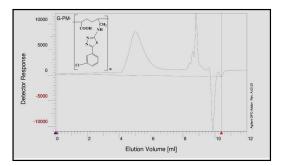


Fig. 2. GPC for P1



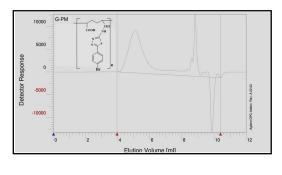
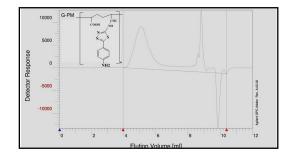


Fig. 4. GPC for P3





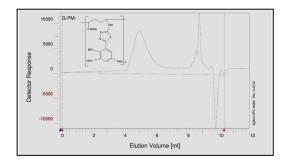


Fig. 6. GPC for P5

C. Thermal gravimetric analysis (TGA)

In general, among the prepared polymers P_2 , P_1 , P_5 were stable up to 100 degrees while P8 and P1 were of higher stability, reaching about 120 degrees. The P_2 polymer was observed in three areas that witnessed a decrease or loss in weight: the first, which extended from 100-140 degrees, which caused a decrease in weight of approximately 12%, which is most likely due to the loss of the carboxyl group, which is concentrated along the chain outside the ring structures. As for the second region, it witnessed a decrease in weight of 38%, in the range of temperatures from 140-280 degrees, which can be attributed to the release of groups of us to chlorine in the form of chlorine gas or hydrogen chloride gas, which was accompanied by a heat-emitting reaction as a result of polymer combustion, and as the summit appeared at 140 degrees, which also paves the way for a 22% reduction in weight after the temperature increased to nearly 480 degrees. The polymer P3 did not differ much from the polymer P₂ except that an increase in stability was observed to approximately 120°C and a weight reduction of 10% in the range 120-135°C. The change is at 120 degrees. The greatest reduction in weight, which reached 60% at a temperature of 130-275 degrees, and this other can be attributed to the exit of bromine groups in the form of bromine gas or hydrogen bromide. The polymer P₄ was also somewhat identical to the two previous polymers, as well as the other two polymers, and the most prominent distinguishing feature of it from the rest of the polymers was the heat-emitting reaction at the temperature of 130, which was associated with the first decrease in weight in the range 120-230 degrees, with a ratio of approximately 10% for the carboxyl group. Then the weight is reduced

to about 20% and the yield of the amine group, which is most likely to be produced in the form of ammonia gas, at a temperature of 360-470. As for the remainder of the material after burning, it was approximately 18%, which is more closely related to the rest of the polymers. The polymer P₁ is very similar to the polymer, P₂, except for a simple gap in proportions that did not exceed 2% with the release of nitrogen oxide in the region that witnessed a reduction in weight of approximately 32% in the range 280-500 degrees, noting that the remainder after combustion did not exceed 7%. The polymer P₅ showed the same first point of reduction in weight belonging to the carboxyl group, then two areas of reduction in the first weight from 200-300 with a reduction rate of 40% and the second was from 300-450, which showed a reduction of approximately 30% of the polymer and its transformation into residues of no more than 12 %.





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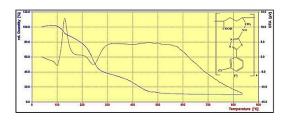


Fig. 8. TGA for P₂

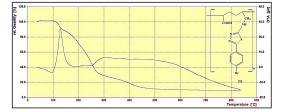
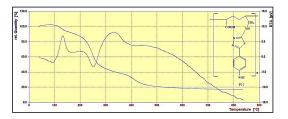


Fig. 9. TGA for P₃



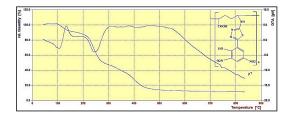


Fig. 11. TGA for P5

D. Photostabilization

A 5ml solution composed from dissolving 5g PVC in THF 100 ml, was mixed with 0.05g from the copolymers (P_1-P_5) and the mixture stirred until the components are fully dissolved and then the mixtures were poured on glass slides and left 24 hours [20]. The films were irradiated with UV light 254 nm for 300 h.

E. Adhesion strength

Copolymers (P_1-P_5) 0.1g were dissolved in THF 3ml. Take 0.5 ml from the above solution and put it on the cellulose paper. The dimensions of the paper are (4 cm, 20 cm) and another sheet of cellulose of the same dimensions was placed and the paper was left to dry at room temperature for 24 h method single-lap shear testing [21].

F. Solubility

The solubility of synthesized copolymers were tested against some solvents such as dimethyl sulfoxide (DMSO), tetra hydro furan (THF), N,N-dimethyl foramide (DMF), benzene, water ,methanol, ethanol, acetone, 10% (w/v) potassium hydroxide (KOH) [22]. The solubility were test conducted by dissolving 0.1 g of the polymer under study in 5 ml of the solvent mentioned above.

III. RESULTS AND DISCUSSION

A. Acrylic acid-Co-N-(substitutedphenyl-1,3,4 thiadia*zole*) acryl methylamine copolymer (P_1 - P_5).

The synthesis involved the reaction of an appropriate carboxylic acid with thiosemicarbazide in the presence of POC13 followed by reflux with water to form compounds (A_1-A_5) . The compounds (A_1-A_5) were reacted with allyl chloride in the presence of DMF to form (B_1-B_5) . The (B_1-B_5) were reacted with acrylic acid in the presence of AIBN to from (P_1-P_5) . All the synthesized compounds were characterized by their melting point, F.T.IR and ¹H-NMR.

В. **Photostabilization**

The efficiency of synthesized copolymers (P_1-P_5) as photostabilizers for PVC [23] was found to be as follows:- $P_4 > P_1 > P_2 > P_3 > P_5 > PVC$ Table (2): Carbonyl index $(I_C=O)$ with irradiation time for PVC films containing from addition 0.5% additives.

GPC ACTUAL FACTORS OF POLYMERS (P1-P5).							
Polymer	Irradiation time (h)						
	0	50	100	150	200	250	300
PVC (blank)	0	0.18	0.23	0.25	0.54	0.79	0.93
PVC+P1	0	0.46	0.62	0.78	0.98	1.23	1.3
PVC+P2	0	0.38	0.51	0.72	0.95	1.15	1.2
PVC+P3	0	0.67	0.72	0.81	0.93	0.99	1.15
PVC+P4	0	0.78	0.89	0.99	1.19	1.23	1.35
PVC+P5	0	0.46	0.62	0.78	0.98	1.23	1.3

TABLE 2

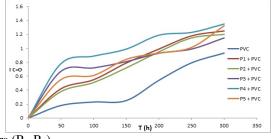


Fig. 12. Carbonyl index for copolymers (P_1-P_5)

C. Adhesion strength

The adhesion strength for the synthesized polymers was measured using single-lap shear method [24]. The

values of adhesion strength for the synthesized polymers are listed.

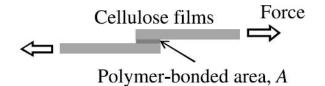


Fig. 13. Single-lap shear testing

	TABLE 3 THE SYNTHESIZED POLYMERS (P_1 - P_5).
Polymer No.	Adhesion Strength
P1	74.15 N.m ²
P2	116.6 N.m ²
P3	196.3 N.m ²
P4	159 N.m ²

95.3 N.m²

D. Solubility

The polymers exhibit different solubility against the used solvent [25].

TABLE 4 THE SOLUBILITY WITH DIFFERENT SOLVENT

Polymer No	THF	DMF	DMSO	Benzene	Acetone	Methanol	ethanol	water	10%(w/v) KOH
P1	++	+	+++	++	+	_	_	_	+++
P2	++	+	+++	++	+	_	_	_	+++
P3	++	+	+++	+	++	_	_	_	+++
P4	++	+	+++	++	+	_	_	_	+++
P5	++	+	+++	++	+	_	_	_	+++

Highly soluble (+++), Moderate soluble (++), low soluble (+), In soluble _

P5

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