

Research Article

Microwave-Assisted Synthesis of Cross-Linked Co-poly(itaconic anhydride-methyl methacrylate): The Effects of the Molar Ratio and Cross-Linking Agent on the Thermal Stability

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In the present work, a new series of cross-linked copolymers based on itaconic anhydride and methyl methacrylate were prepared employing free radical copolymerization in the presence of azobisisobutyronitrile as an initiator and 2-butanone as a solvent under microwave irradiation. The copolymers containing itaconic anhydride (ITA) and methyl methacrylate (MMA) were chosen due to the formation of long-term stable anhydride moieties, which might be useful to attach enzymes covalently with numerous applications in water treatment. The copolymerization process was carried out in the presence of two types of cross-linking agent, namely, ethylene dimethacrylate (EDMA) and divinylbenzene (DVB) in a range of 0-20% (*w/w*) to explore their effect on the thermal and stiffness properties of the obtained cross-linked copolymers. Increasing the ratio of the cross-linking agent, the copolymers prefer to precipitate rather than form a gel during the polymerization process. While using ethylene dimethacrylate as a cross-linking agent, the copolymers change from porous to stiffness structures depending on the molar ratio of the monomers used during the polymerization. On the other hand, using divinylbenzene as a cross-linking agent, the stiffness structure was obtained in all cases and there is no effect observed for the monomer's ratio or the percentage of cross-linking agent on the morphology of the prepared copolymers.

1. Introduction

Microwave irradiation has become a common heat source in organic chemistry [1–5]. Inspired by this enormous success, the use of microwave irradiation is also recently increased for polymerization reactions [6–9]. The use of microwave irradiation in polymerization reactions enhanced the reactivity and selectivity as well as improves the reaction yield and the properties of the as-obtained polymers [2, 3, 7–10]. In addition, improving the overall properties of polymers such as their thermal and mechanical properties is a critical challenge in both their synthesis and applications [11].

The synthesis of cross-linked polymers is one way to improve the thermal and mechanical properties of polymers; the cross-linking density in the polymer network and the molecular weight of the polymers between the crosslinking points have an effect on the properties of cross-linked polymers [12–14].

Cross-linked polymers can be prepared via chemical (covalent or ionic bonds) or physical (hydrogen bonds, Van der Waals, or other interactions) cross-linking [12]. Chemical cross-linking polymerization is usually carried out in the presence of cross-linking agents to prepare highly cross-linked polymers with different degrees of cross-linking [14].

Itaconic anhydride (ITA) can be obtained from renewable resources such as plants produced from the fermentation of carbohydrates, which forms itaconic acid that can be converted into anhydride via dehydration or by the pyrolysis of citric acid [15]. Polymers and copolymers based on ITA can be prepared via free radical reaction polymerization [16–21].

In addition, ITA has extensively been used in industrial applications as comonomer, for instance, as an essential for rubber materials, paints and colors, coatings, biodegradable polymers, contact lenses, or medicinal applications [22, 23]. The anhydride groups exist in the copolymers containing

ITA normally used to immobilize enzymes *via* the reaction of amino groups with the anhydride-containing copolymer [24–30]. Itaconic anhydride (ITA) has been also used as a monomer with various vinyl monomers such as vinyl chloride [31–33], acrylonitrile, vinyl acetate, 2-chloroethyl acrylate [31, 34], and styrene [33–35]. Moreover, Miles et al. [20] reported that poly(ITA) exhibited good adhesion to silicon surfaces and behaved as a positive-acting electron-beam resist material [20]. The same authors [31] reported the synthesis of thermally cross-linked methyl methacrylate- (MMA-) based copolymer, containing ITA, which was investigated as alternative thermally cross-linkable resist material [31].

In addition, methyl methacrylate (MMA) comonomer provides mechanical stability for the copolymer and chemical resistance against a number of organic solvents. Furthermore, it has advantages of poly(methyl methacrylate) (PMA), which is considered to have good adhesion to different surfaces and the transparency coating [36].

Accordingly, the present work represents the synthesis of a new series of cross-linked copolymers based on different ratios of ITA and MMA using a microwave irradiation. Samples of copolymers were prepared using various types of cross-linking agents and different degrees of crosslinking to explore their effect on the thermal properties and the morphology of the as-obtained cross-linked polymers. Two types of cross-linking agents, ethylene dimethacrylate (EDMA) and divinylbenzene (DVB), were used with the degree of cross-linking in the range of 0–20% (*w/w*). The structure, thermal properties, and surface morphology of the cross-linked polymers were also studied.

2. Materials and Methods

Methyl methacrylate (MMA), itaconic anhydride (ITA), ethylene dimethacrylate (EDMA), divinylbenzene (DVB), and *N,N'*-azobisisobutyronitrile (AIBN) were supplied from Sigma-Aldrich (Chemie GmbH, 82024 Taufkirchen, Germany). AIBN was recrystallized from absolute ethanol prior to use. All solvents were dried before use.

A microwave (Monowave 300, Aton Paar GmbH, 1400 W maximum magnetron, Germany) with a maximum filling volume of 6 and 20 mL for 10 and 30 mL vials, respectively. Maximum operating pressure of 30 bar, maximum IR temperature of 300°C, maximum fibre-optic temperature of 300°C, and maximum power of 850 W were used. The vials were constructed from borosilicate glass and silicon carbide using PEEK caps and Teflon-coated silicone seals.

2.1. Characterization. The functional groups of the prepared cross-linked copolymers were investigated by Fourier-transform infrared (FT-IR) spectroscopy. The thermal properties were studied using thermogravimetric analysis (Q500 TGA, USA) under nitrogen atmosphere within the temperature range 30 to 800°C and at the heating rate 10°C/min. The morphology of the prepared copolymers was studied using scanning electron microscopy (SEM). The specific surface area and the pore size distribution were investigated by applying Brunauer-Emmett-Teller (BET) theory and

Barrett-Joyner-Halenda (BJH) model using Micromeritics (ASAP-2020, USA) at the temperature 77 K.

2.2. General Procedure for Copolymer Synthesis. Cross-linked copolymers were prepared using microwave-assisted method (Monowave 300, Anton Paar) as described elsewhere [37, 38]. In a typical reaction, itaconic anhydride (ITA) was mixed with methyl methacrylate (MMA) at different molar ratios in the presence of 5% (*w/w*) AIBN using 2-butanone (6 mL) as solvent and different amounts of EDMA or DVB as the cross-linking agent (5, 10, 15, and 20%, *w/w*) in 20 mL reaction vial, as shown in Table 1. The individual vials were fixed by screwing down the upper rotor plate and finally closed with the protective hood. The reaction vials were heated to 120°C for 5 min, were held at the same temperature for 5 min (~12–13 bar pressure, 5–6 W), and then were cooled using a fan for 5 min.

The precipitated final products, DPMITA 1-5, EPMITA 1-5, EPMITA 1-10, EPMITA 1-15, and EPMITA 1-20, were washed with diethyl ether and dried in a vacuum oven at 40°C for 24 h.

The other final products, DPMITA 1-10, DPMITA 1-15, and DPMITA 1-20, were washed with acetone, and dried in a vacuum oven at 40°C for 24 h.

3. Results and Discussion

3.1. Copolymer Synthesis. Various copolymer compositions can produce a very large number of different arrangements, producing materials of varying chemical and physical properties. Thus, the hydrophilicity of copolymers can be modified by changing the amount of incorporated itaconic anhydride [22]. These amphiphilic polymers, at which the copolymers contain both hydrophilic and hydrophobic segments, have considerable attention in different applications as in biological systems [27], medicinal chemistry [30], water treatment, and heavy metal removal [39].

Different ratios of itaconic anhydride (ITA) and methyl methacrylate (MMA) were mixed in 2-butanone as solvent in the presence of AIBN (5%) as an initiator for 5 min at 120°C using a microwave-assisted free radical copolymerization (Scheme 1).

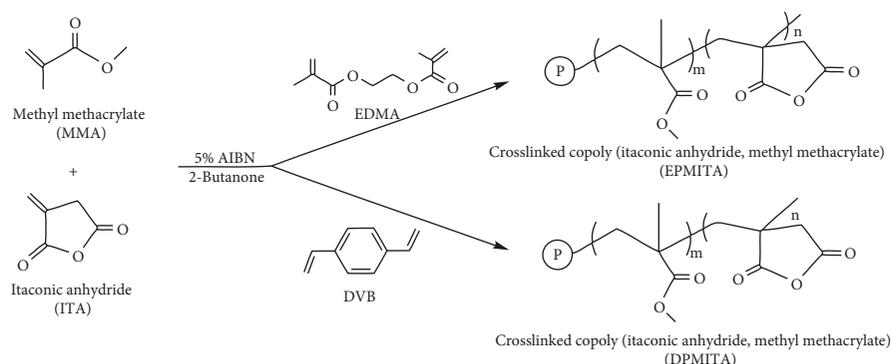
It was noticed that the polymer preferred to form a precipitate rather gel during the copolymerization process upon increasing the ratio of the cross-linking agent at a monomer ratio of MMA : ITA = 1 : 2 using EDMA as the cross-linking agent and with monomer ratio of (MMA : ITA = 1 : 1) using DVB as crosslinking agent (Figures 1 and 2, respectively). Moreover, formation of precipitated copolymer rather than the gel is favoured during the reaction upon increasing the amount of MMA in the copolymer (Figure 2).

3.2. FT-IR Spectroscopy and Elemental Analysis. The FTIR spectra of the different compositions of ITA and MMA (EPMITA and DPMITA) in the presence of different cross-linking agents ethylene dimethacrylate and divinylbenzene were studied. The copolymer ITA-MMA (EPMTITA) using ethylene dimethacrylate showed characteristic bands at 1863 and 1783 cm⁻¹ for ITA (C=O) (symmetric and

TABLE 1: Summary of the copolymer's ratio and yield.

Copolymer code	Cross-linking agent (%/g)	MMA/ITA ratio	MMA (g/mmol)	ITA (g/mmol)	AIBN* (g)	Yield (g)
EPMITA 1-5	5/0.1621				0.1702	0.85
EPMITA 1-10	10/0.3243	1 : 2	1.0012/10	2.2416/20	0.1784	2.56
EPMITA 1-15	15/0.4864				0.1864	2.15
EPMITA 1-20	20/0.6486				0.1945	1.80
EPMITA 2-15	15/0.3183	1 : 1	1.0012/10	1.1208/10	0.1220	1.70
EPMITA 2-20	20/0.4244				0.1273	1.90
EPMITA 3-15	15/0.4685	2 : 1	2.0024/20	1.1208/10	0.1795	2.10
EPMITA 3-20	20/0.6246				0.1874	2.84
DPMITA 1-5	5/0.1621				0.1702	1.20
DPMITA 1-10	10/0.3243	1 : 2	1.0012/10	2.2416/20	0.1784	2.80
DPMITA 1-15	15/0.4864				0.1864	1.80
DPMITA 1-20	20/0.6486				0.1945	2.52
DPMITA 2-5	5/0.1061	1 : 1	1.0012/10	1.1208/10	0.1114	1.60
DPMITA 2-10	10/0.2122				0.1167	1.80
DPMITA 3-5	5/0.1562	2 : 1	2.0024/20	1.1208/10	0.1717	2.20
DPMITA 3-10	10/0.3123				0.1717	2.40

*5% (w/w).



SCHEME 1: Copolymerization of itaconic anhydride and methyl methacrylate in the presence of ethylene dimethacrylate (EDMA) and divinylbenzene (DVB) as cross-linking agents.

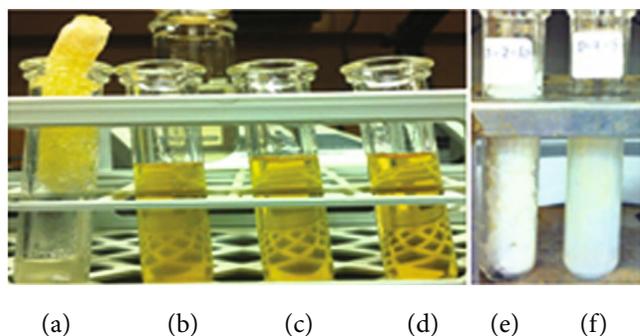


FIGURE 1: Photograph of the (a) EPMITA 1-20, (b) EPMITA 1-15, (c) EPMITA 1-10, (d) EPMITA 1-5, (e) DPMITA 2-5, and (f) DPMITA 2-10 copolymers.

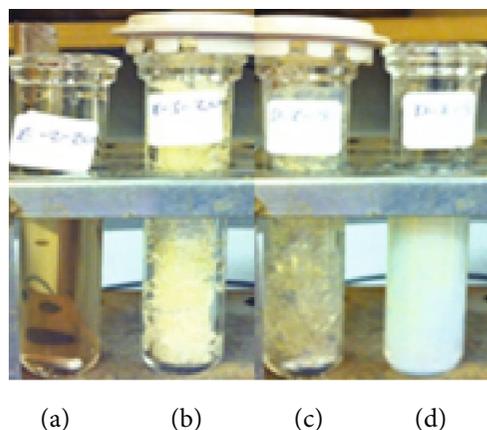


FIGURE 2: Photograph of the (a) EPMITA 2-20, (b) EPMITA 3-20, (c) DPMITA 3-5, and (d) DPMITA 2-5 copolymers.

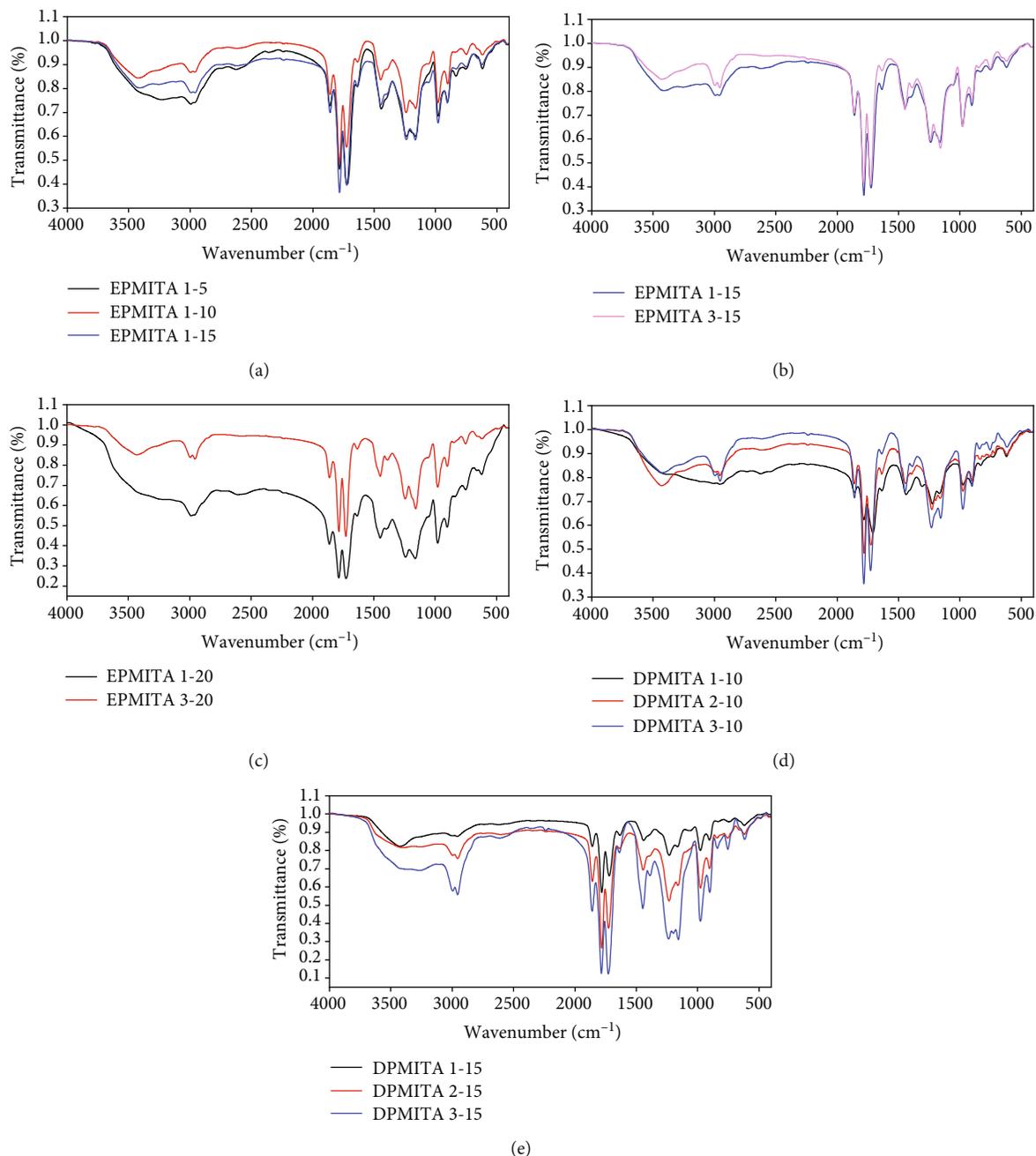


FIGURE 3: FT-IR of EPMITA and DPMITA copolymers: (a) EPMITA 1-5, EPMITA 1-10, and EPMITA 1-15; (b) EPMITA 1-15 and EPMITA 3-15; (c) EPMITA 1-20 and EPMITA 3-20; (d) DPMITA 1-10, DPMITA 2-10, and DPMITA 3-10; (e) DPMITA 1-15, DPMITA 2-15, and DPMITA 3-15.

asymmetric stretching of the carbonyl in the 5-membered anhydride ring) and $1724\text{--}1728\text{ cm}^{-1}$ for the stretching carbonyl group of the ester corresponding to MMA residue, beside a characteristic band at 1640 cm^{-1} related to the stretching C=O ester of the cross-linking agent (EDMA) (Figures 3(a)–3(c)). The intensity of the cross-linking agent was increased as the ratio increased as observed from Figures 3(a)–3(c) (Table 2). The copolymer MMA-co-ITA (DPMITA) using DVB as cross-linking agent showed the same characteristic bands at 1863 and 1782 cm^{-1} for ITA (C=O) (symmetric and asymmetric stretching of the

carbonyl in the 5-membered anhydride ring) and $1709\text{--}1728\text{ cm}^{-1}$ for the stretching carbonyl group of the ester corresponding to MMA residue, beside a characteristic band at $1631\text{--}1640\text{ cm}^{-1}$ related to the stretching CH=CH aromatic related to the cross-linking agent (DVB) (Figures 3(d)–3(e), Table 2).

The FTIR of ITA-MMA copolymers' results indicated that during the microwave process, the itaconic anhydride moieties were not disrupted in the copolymer backbone chain, which is in accordance with the previously reported data [15, 27].

TABLE 2: FT-IR peaks observed for the EPMITA and DPMITA copolymers.

Functional group	Peak assignment	Wavenumber (cm ⁻¹)	
		EPMITA copolymers	DPMITA copolymers
Aliphatic	C-H stretching of methyl	2955-2958	2954-2957
	Aliphatic backbone stretching	1437-1451	1438-1449
Carbonyl group	C=O stretching (anhydride) (C=O symmetric and asymmetric)	1783-1863	1780-1782
	C=O stretching methyl methacrylate	1724-1728	1709-1728
	C=O stretching (ester) EDMA	1636-1640	—
Ether	Stretching vibration of C-O-C	1160-1242	1155-1232
Aromatic	Aromatic C-H stretch	—	2995-3004
	Aromatic =CH stretch	—	1631-1640
	Aromatic =CH bending	—	618-899

TABLE 3: Information derived from the TGA of the degradation of the EPMITA and DPMITA copolymers.

Copolymer code	Distribution of volatile ranges (temperature range) (°C)				T_{onset} (°C)	T_{max} (°C)	T_{50} (°C)	Residue (%) [*]
	30-150	150-230	230-349	349-600				
EPMITA 1-5	30-150	150-230	230-349	349-600	168	248	340	17.13
	6.7%	17.7%	27.0%	32.2%				
EPMITA 1-10	30-142	142-229	229-339	339-600	228	387	377	18.88
	4.0%	12.4%	26.6%	37.9%				
EPMITA 1-15	30-137	137-225	225-331	331-600	244	390	371	13.80
	2.7%	14.1%	25.2%	43.7%				
EPMITA 1-20	30-99	99-215	215-342	342-600	254	399	394	12.13
	0.7%	13.8%	25.7%	47.7%				
EPMITA 2-15	30-100	100-231	231-329	329-600	231	388	381	11.00
	1.4%	10.9%	25.1%	51.3%				
EPMITA 2-20	30-100	100-235	235-329	329-600	236	390	385	9.75
	1.1%	12.9%	23.0%	52.9%				
EPMITA 3-15	30-100	100-149	149-323	323-600	222	380	380	8.80
	0.5%	2.3%	29.3%	59.7%				
EPMITA 3-20	30-100	100-326	326-600	253	387	390	7.29	
	0.6%	30.9%	61.2%					
DPMITA 1-5	30-164	164-231	231-345	345-600	188	401	384	18.84
	6.3%	11.1%	25.5	38.0%				
DPMITA 1-10	30-199	199-257	257-350	350-600	140	408	370	16.49
	20.4%	12.1%	14.4	36.5%				
DPMITA 1-15	30-243	243-371	371-600	143	412	422	20.48	
	12.5%	20.3%	46.6%					
DPMITA 2-5	30-200	200-342	342-600	200	396	400	20.30	
	7.5%	28.0%	43.8%					
DPMITA 2-10	30-143	143-341	341-600	212	400	399	16.56	
	11.5%	22.7%	47.3%					
DPMITA 3-5	30-130	130-238	238-329	329-600	238	382	384	12.56
	5.5%	4.8%	22.4	53.1%				
DPMITA 3-10	30-194	194-333	333-600	263	391	398	14.14	
	1.8%	25.3%	54.7%					

*At 600°C.

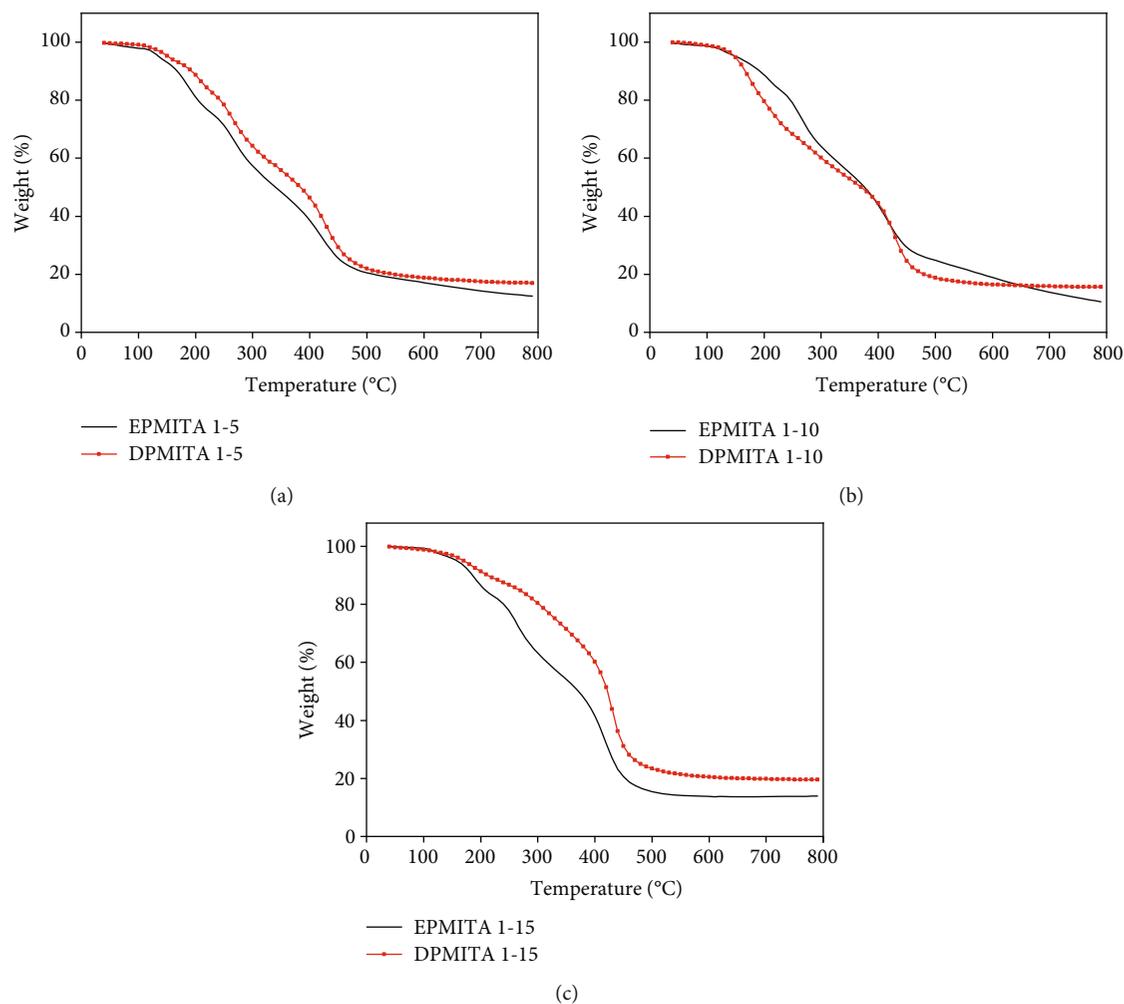


FIGURE 4: TGA curves recorded for the different copolymers: (a) EPMITA 1-5 and DPMITA 1-5; (b) EPMITA 1-10 and DPMITA 1-10; (c) EPMITA 1-15 and DPMITA 1-15 showing the effect of the type of cross-linking agent used.

3.3. Thermogravimetric Analysis. Thermogravimetric analysis of the prepared copolymers is shown in Table 3 and Figures 4 and 5. Degradation takes place in four steps for copolymers EPMITA 1-5, EPMITA 1-10, EPMITA 1-15, EPMITA 1-20, EPMITA 2-5, EPMITA 2-10, EPMITA 2-15, EPMITA 2-20, EPMITA 3-5, EPMITA 3-10, EPMITA 3-15, DPMITA 1-5, DPMITA 1-10, and DPMITA 3-5 and in three steps for copolymers EPMITA 3-20, DPMITA 1-15, DPMITA 2-5, DPMITA 2-10, and DPMITA 2-10. It was observed that the first step might be attributed to the evaporation of residual water and decarboxylation of the anhydride groups [15]. The next steps involve the degradation of the ester linkages in the side chains, followed by the degradation of the cross-linking agent [15]. Finally, the copolymer backbone is degraded generally at $>300^{\circ}\text{C}$ leaving a residue at 600°C of 7.3-18.9 and 12.6-20.5% for the EPMIA and DPMITA copolymers, respectively. The amount of residue depends on the copolymer composition as well as the type of cross-linking agent used. The DPMITA copolymers show higher residue due to the use of an aromatic cross-linking agent.

3.4. Effect of the Type of Cross-Linking Agents. The EPMITA copolymers showed high thermal stability when using $>10\%$ (w/w) of the cross-linking agent, and the decomposition was independent of the ITA content. Moreover, the thermal stability was $251\text{-}3^{\circ}\text{C}$ and the maximum degradation of the copolymers was in the range of $380\text{-}399^{\circ}\text{C}$, which was not affected by the copolymer composition. The thermal stability reached a maximum at 258°C for the EPMITA 2-20 copolymer containing 20% (w/w) of the cross-linking agent. The copolymer composition may affect the amount of residue, which increased upon increasing the ITA content and decreasing the amount of cross-linking agent used.

On the other hand, the thermal stability of the DPMITA copolymers is affected by the copolymer composition as well as the percentage of cross-linking agent used. A significant increase in the thermal stability was observed upon increasing the ITA content with the onset temperature increasing from 140 to 212°C , reaching a maximum at 263°C for the DPMITA 1-10, DPMITA 2-10, and DPMITA 3-10 copolymers, respectively. The same results, obtained for DPMITA

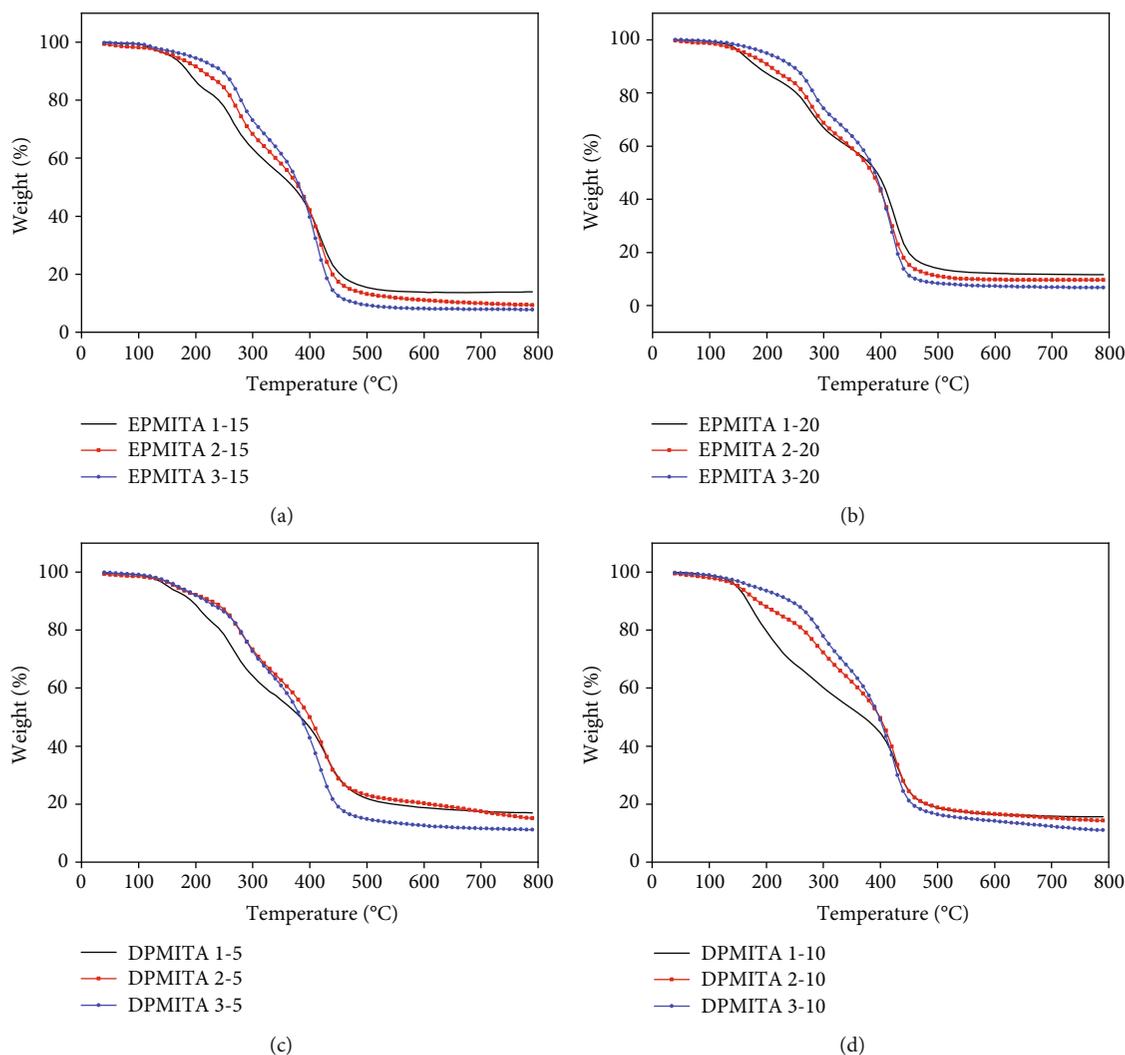


FIGURE 5: TGA curves recorded for the different copolymers: (a) EPMITA 1-15, EPMITA 2-15, and EPMITA 3-15; (b) EPMITA 1-20, EPMITA 2-20, and EPMITA 3-20; (c) DPMITA 1-5, DPMITA 2-5, and DPMITA 3-5; (d) DPMITA 1-10, DPMITA 2-10 and DPMITA 3-10 showing the effect of the monomer molar ratio used.

1-5, DPMITA 2-5, and DPMITA 3-5, made clear that the thermal stability decreased upon increasing the percentage of cross-linking agent used.

3.5. SEM for Copolymers. The morphological structures of the copolymers EPMITA 1-15, EPMITA 2-15, and EPMITA 3-15, EPMITA 1-20, EPMITA 2-20, EPMITA 3-20 (Figure 6), DPMITA 1-5, DPMITA 2-5, and DPMITA 3-5, DPMITA 1-10, DPMITA 2-10, and DPMITA 3-10 were observed using SEM (Figure 7).

In regard to series A (Figure 6), by changing the molar ratio of the monomers used MMA/ITA from 1:2 to 1:1, porous structures were obtained, while by increasing the amount of MMA (EPMITA 3-15) in the copolymer, the porosity decreased leading to stiffness structures, which may be attributed to the postcross-linking process in the copolymer. This structure was formed because MMA is a good candidate for the cross-linking process, which is observed as rapid precipitation during the copolymer synthesis [27].

On the other hand, from series A to series B (Figure 7), the roughness increases upon increasing the percentage of cross-linking agent (EDMA) used from 15 to 20% (w/w), which indicates the presence of a high degree of cross-linking in the copolymer.

In the case of using DVB as the cross-linking agent, stiffness structure was formed in all cases and there was no effect due to the monomer ratio or the percentage of cross-linking agent used on the morphology of the as-prepared copolymers [40, 41].

3.6. Surface Area and Pore Size Analysis. According to the SEM images, EPMITA 1-15 and EPMITA 2-15 showed a porous structure. Therefore, both samples were selected to analyse the surface area and type of pores and pore volume by BET. The BET surface area and pore size distribution are displayed in Figure 8. The specific surface areas of EPMITA 1-15 and EPMITA 2-15 are determined to be 1.04 and 1.18 m^2/g , respectively; whereas the pore volumes are 0.0063 and 0.017 cm^3/g , respectively. This result is consistent

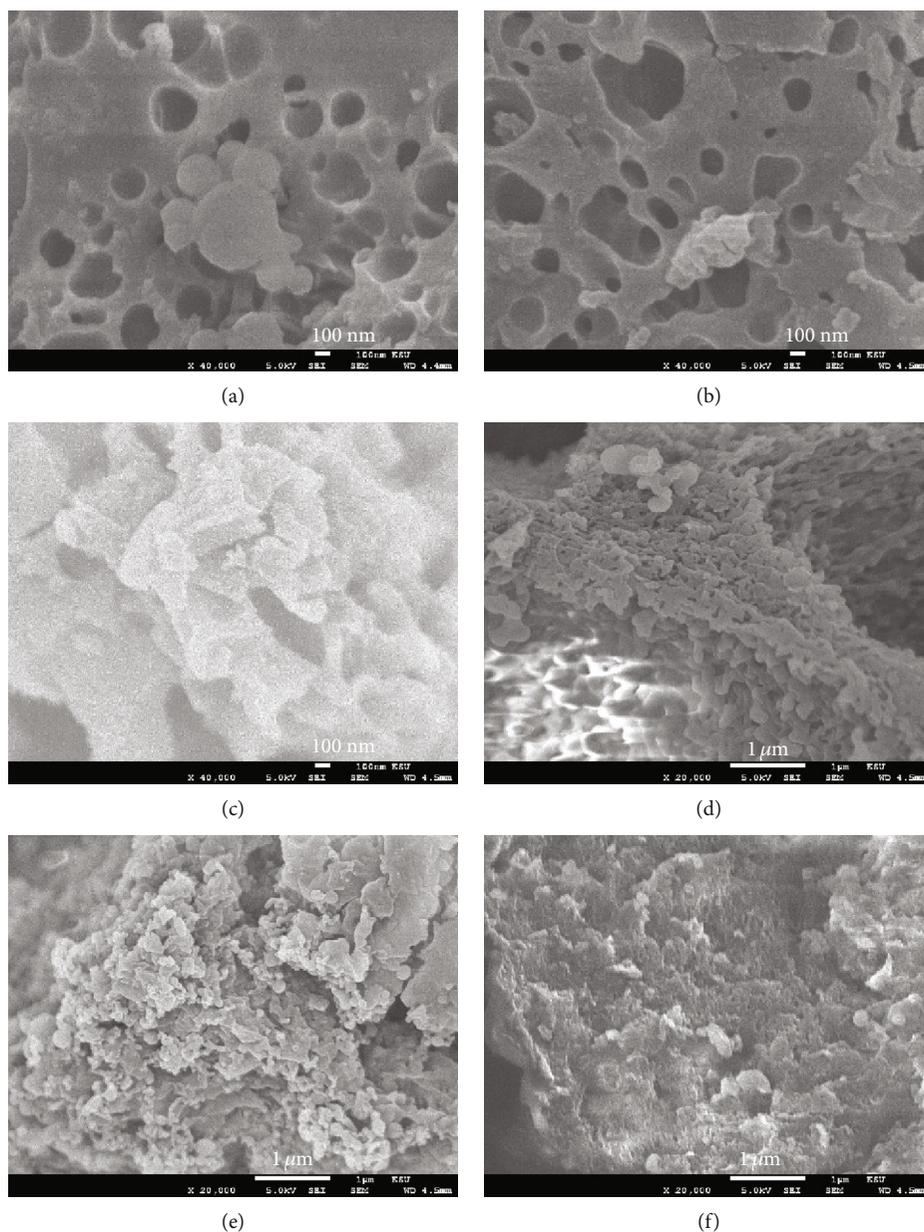


FIGURE 6: SEM images of the different copolymers: (a) EPMITA 1-15, (b) EPMITA 2-15, (c) EPMITA 3-15, (d) EPMITA 1-20, (e) EPMITA 2-20, and (f) EPMITA 3-20 showing the effect of the monomer molar ratio, type, and percentage of the cross-linking agent used.

with the SEM images, which have proved that the structure of EPMITA 2-15 was more porous than EPMITA 1-15. The analysis of pore size distribution by the Barrett-Joyner-Halenda (BJH) method [42] showed that EPMITA 1-15 and EPMITA 2-15 have a mesoporous and macroporous structure. The pore size distribution of both samples has a wide range from 2 to 90 nm with the average pore sizes 26.6, and 25.3 nm for EPMITA 1-15 and EPMITA 2-15, respectively.

3.7. Prospective Applications. The above-going discussions and the results obtained for EPMITA 1-15 and EPMITA 2-15 copolymers indicate that these possess a mesoporous and macroporous structure with average pore sizes of 26.6,

and 25.3 nm, respectively. Hence, these obtained data could be useful for application in water purification technology.

4. Conclusions

Cross-linking has been used to improve the solubility, stiffness, mechanical strength, and rigidity of polymers for some potential applications. Itaconic anhydride-based copolymers were prepared with methyl methacrylate in the presence of two types of cross-linking agents, EDMA and DVB, via a microwave-assisted synthesis. The FTIR results indicated that the microwave process did not disrupt the itaconic anhydride moieties in the copolymer backbone chain. The formation of a cross-linked copolymer is favoured rather than a gel

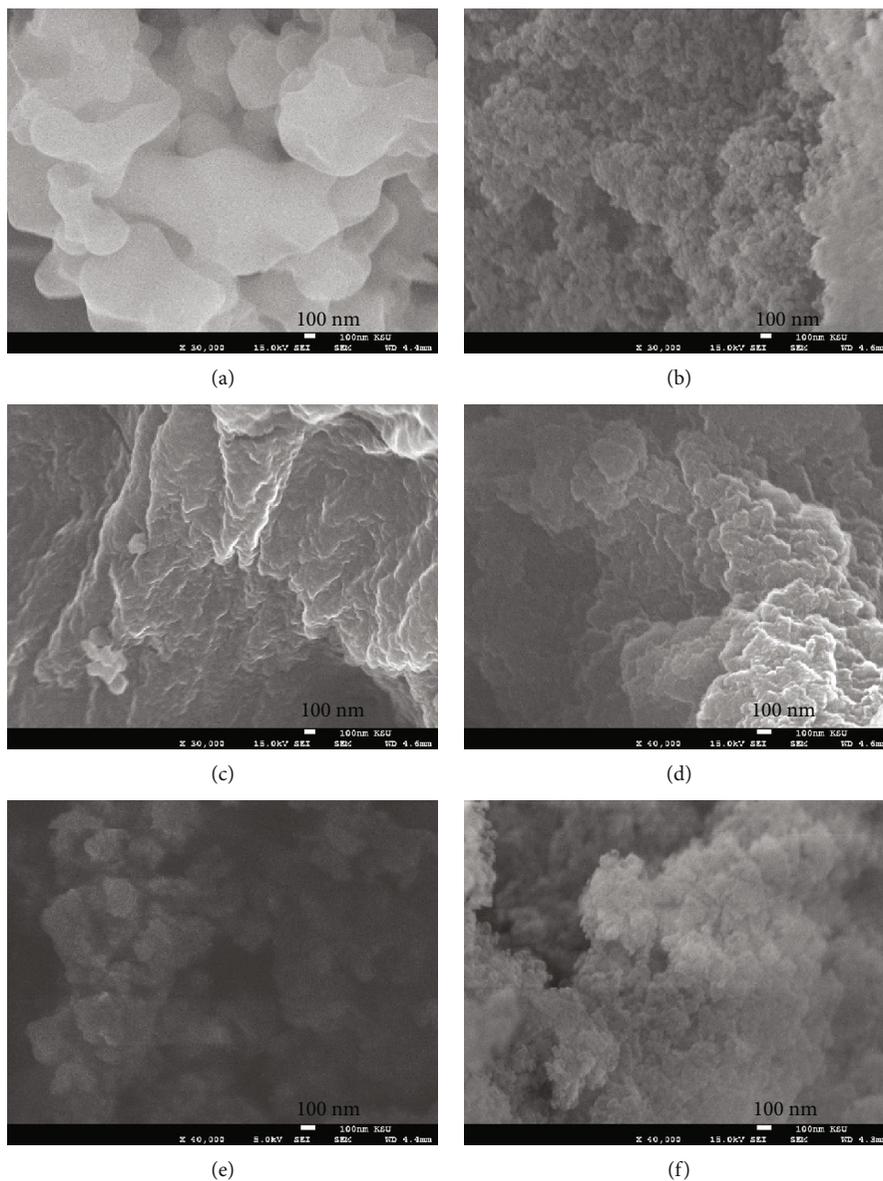


FIGURE 7: SEM images of the different copolymers: (a) DPMITA 1-5, (b) DPMITA 2-5, (c) DPMITA 3-5, (d) DPMITA 1-10, (e) DPMITA 2-10, and (f) DPMITA 3-10 showing the effect of the monomer molar ratio, type, and percentage of the cross-linking agent used.

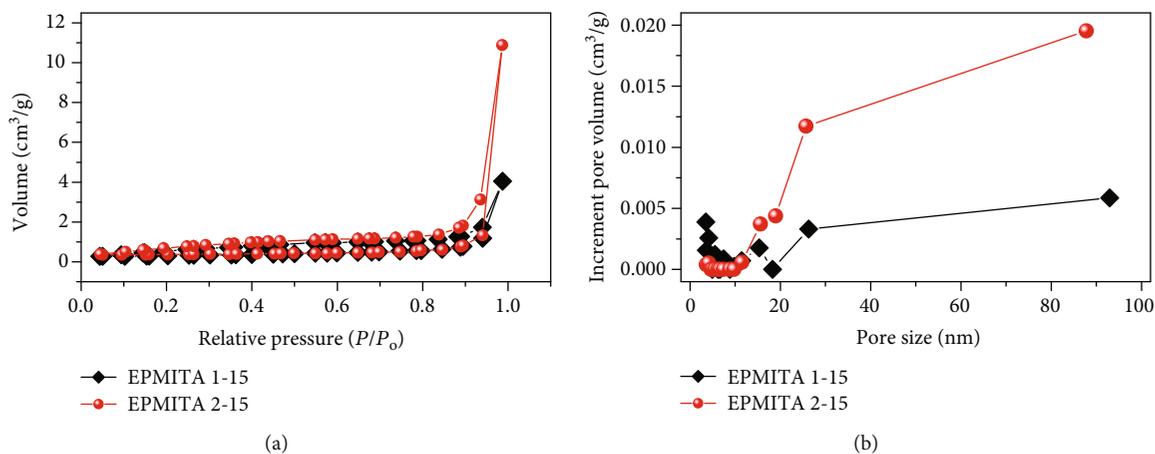


FIGURE 8: (a) N₂ adsorption/desorption isotherms and (b) pore size distribution by the BJH method.

during the polymerization process upon increasing the amount of MMA in the copolymer. The EPMITA copolymers show high thermal stability when prepared using >10% (*w/w*) of the cross-linking agent, and its decomposition was independent of the ITA content. For the DPMITA copolymers, the thermal stability increased upon increasing the ITA content. The prepared copolymers showed different morphological structures depending on the monomer ratio and type of cross-linking agent used. EPMITA 1-15 and EPMITA 2-15 have porous structures and become stiff upon increasing the ratio of MMA in the copolymer (EPMITA 3-15). For the DPMITA copolymers, there was no effect due to the monomer ratio or the percentage of DVB used on the morphology of the as-obtained copolymers, which all showed a stiffness structure. In general, stiffness structures for the copolymers are observed upon increasing the percentage of cross-linking agent used. Moreover, EPMITA 1-15 and EPMITA 2-15 have a mesoporous and macroporous structure with average pore sizes of 26.6, and 25.3 nm, respectively. These data obtained could be useful for some applications in water purifications.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The author declares that there is no conflict of interest.

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