



The Effect of Poly (Propylene Glycol – g – Styrene) on the Physicomechanical Properties of Unsaturated Polyester Resin

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Abstract

Unsaturated polyester resin (UPR) is a thermoset-type polymer, and it is widely used in the fiber-reinforced plastic industry. This can be attributed to its low cost, ease of processing and combination with reinforcements, rapid cure, excellent dimensional stability, and a wide variety of grades available. This study was conducted to investigate the effect of grafted copolymers on the properties of UPR. Testing included viscosity, gel time, curing temperature, hardness, tensile strength, and compressive strength. The grafted copolymers were based on polypropylene glycol (PPG) grafted with styrene (St) at different St ratios (65/15, 65/25, 65/35). The grafted copolymers were prepared by free-radical polymerization in the presence of potassium persulphate as an initiator. The results showed that significant improvement in the physical and mechanical properties of UPR due to the modification of UPR by the prepared grafted copolymer. It was found that the physical and mechanical properties of UPR enhanced with increasing the ratio of St in the grafted copolymer and the concentration of grafted copolymers. This is attributed to the high rigidity of the grafted copolymer containing the highest styrene content.

Keywords: UPR; grafted; copolymer; polyester; curing

Introduction

An unsaturated polyester resin (UPR) is a macromolecule prepared by the polycondensation reaction of unsaturated and saturated di-acids and diols, with an unsaturated diluent such as styrene [1-6]. The unsaturated di-acid provides sites for cross-linking at the curing stage with styrene. The rate of polyesterification is influenced by the structure and stoichiometry of the glycol and dibasic acid components. The UPR properties are influenced by the choice and proportion of the reactants and the unsaturated co-reactant monomer. In addition, the properties of the cured UPR also depend on the degree of cross-linking, catalyst, and accelerator [5, 6]. The curing of UPR is an exothermic and free radical technique including peroxides such as benzoyl peroxide (BPO) and methyl ethyl ketone peroxide (MEKP) in the presence of accelerators such as N, N dimethyl-p-toluidine and cobalt salt. The UPRs are

used extensively in industrial applications such as tanks, vessels, swimming pools, coatings, plastics, and composites. The properties of UPR can be improved by adding some kinds of additives, including fillers, inhibitors, plasticizers, thixotropic agents, crosslinking agents, and wetting agents [7]. For example, increasing the filler content at a constant styrene/polyester ratio improves the properties of composites, including crack resistance, shrinkage, control viscosity, stiffness and reduce the cost. For gel coat applications, fumed silica or inorganic clay can be used as a thixotropic agent for UPR. Hectorite and other clays can be modified by alkyl quaternary ammonium salts such as di (hydrogenated tallow) ammonium chloride. These organoclays are used in thixotropic unsaturated polyester resin systems. The addition of 2% MgO as a thickener to UPR increased strength from 190 MPa to 340 MPa [7-12]. The compositions of unsaturated

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polyester resin with 2 wt. % of smectites (bentonites) modified with different quaternary ammonium salts showed excellent thixotropic properties and satisfactory fluidity [10]. Diana et al., 2019 investigated the influence of polymeric modifiers of polyvinyl chloride on the physicochemical properties of unsaturated polyester. The results showed that polymer modifier accelerates the process of unsaturated polyester curing, the initial viscosity of polyester increases, and the gel times decreases [13-14]. UPRs were chemically modified by blending with polyurethane prepolymers having terminal isocyanate groups. Properties of the modified UPR, such as tensile strength, toughness, impact resistance, showed considerable improvement [14].

This study investigates the effect of grafted copolymers on the physicomechanical properties of unsaturated polyester (UPR). The grafted copolymers prepared were based on polypropylene glycol (PPG)/ styrene (St) at different styrene (St) ratios [15].

Experimental

Materials

Unsaturated polyester resin (UPR) was supplied by Vaste LLP., Almaty, Kazakhstan. Methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate were purchased from Fluka. Polypropylene glycol (PPG), styrene (St) monomer and potassium persulphate were purchased from Sigma.

Methods

The viscosity (η) of the UPR was measured using a Brookfield viscometer, Spindle 2 at speeds 5 and 50 rpm at 20 °C. The thixotropy index was calculated as:

$$\text{Thixotropy index (TI)} = \eta_5/\eta_{50}$$

The gel-time of UPR films was determined at 25 °C according to the finger-touching method prescribed in KS F 2484. The maximum curing temperature of UPR premixed with grafted copolymers was determined by State Standard (GOST) 21970-2015. Hardness was measured using an indentation Barcol hardness tester according to ASTM B648-10(2015). The tensile properties of the UPR cast films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least four measurements was taken, and the 1-kN load cell was used. The dimensions of the test specimen were (ISO 14125) 60 mm × 15 mm × 2 mm. The compressive strength was determined according to BS EN 12390-3: 2019. Water uptake test was performed according to BS 1881-122:2011. Alkali and acid resistance tests were measured according to DIN 53168: 1982-03.

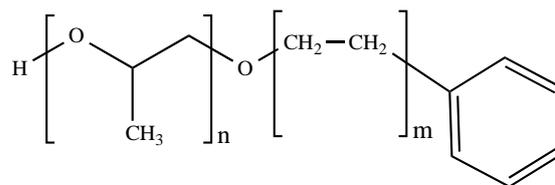
Synthesis and characterization of grafted copolymer (PPG-g-St).

The graft copolymers based polypropylene glycol (PPG) and styrene (St) were synthesized with various ratios of St, i.e. [M1: (65: 15), M2: (65: 25), M3: (65: 35)] using potassium persulphate (KPS) as an initiator and water as solvent at 60 °C for 3 hours. The preparation of grafted copolymers based on Polypropylene glycol (PPG), styrene (St) and the methods of analysis (FTIR, TGA and DSC) has been previously described [15]. The mixed proportion of monomers in the copolymer and basic properties of the prepared copolymers are shown in Table 1. The chemical structure of the grafted copolymer is shown in Scheme 1.

Table 1. Properties of PPG-g-St.

Copolymer	PPG	St	T_g (°C)	T_c (°C)	T_m (°C)	Appearance
M1	65	15	58	112	354	Liquid
M2	65	25	54	114	360	
M3	65	35	51	90	364	

Glass transition temperature (T_g), crystalline temperature (T_c) and melting temperature (T_m) were measured using DSC analysis.



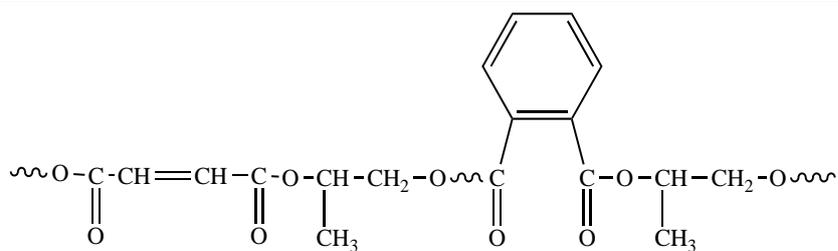
Scheme 1. The chemical structure of PPG-g-St copolymer.

Unsaturated polyester resin (UPR):

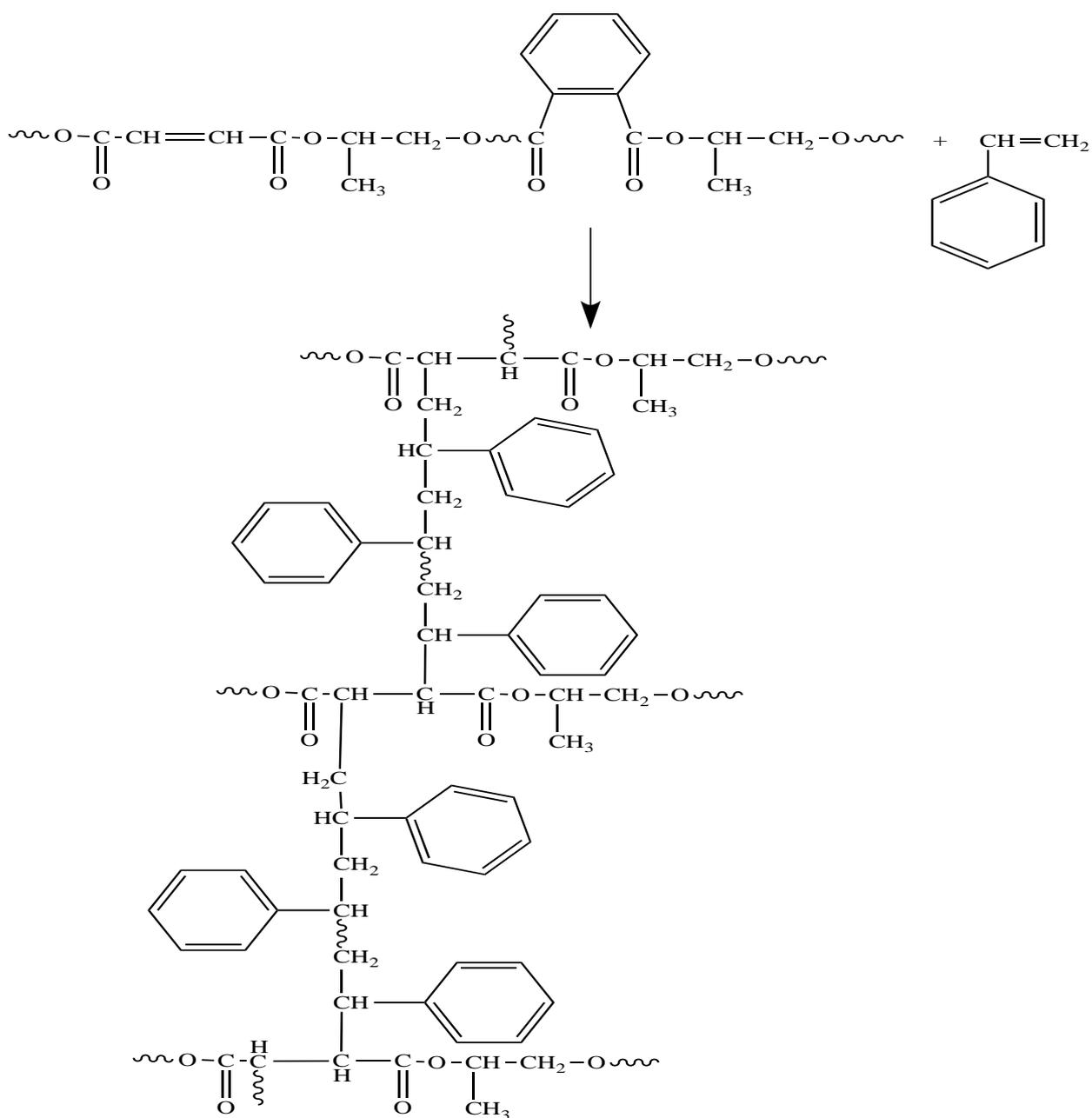
The ingredients of UPR were propylene glycol, diethylene glycol, phthalic anhydride, and maleic anhydride. UPR was a mixture of 60% unsaturated polyester and 40% styrene as solvent. UPR used in the research has a density of 1.12 g/cm³, an acid value of 25 mg KOH/g and solid content of 60%. The chemical structure of the UPR is shown in Scheme 2.

Mixing proportions

15 UPR samples (100 gm) were used to examine the influence of copolymer grafted with different ratios of St and different concentrations of the prepared copolymers on the properties of UPR. UPR and grafted copolymers with different concentrations (1, 2, 3, 4 and 5% based on UPR weight) were mixed in a beaker to produce homogeneous mixtures. UPR mixtures were casted to specimens of dimensions 7 mm x 7 mm x 7 mm cast in steel moulds. The UPR was solidified at room temperature by adding 2 %, by weight of resin, methyl ethyl ketone peroxide initiator and 0.1%, by weight of resin, of cobalt naphthenate promoter (1.2 wt% solution) as shown in Scheme 3.



Scheme 2. The chemical structure of UPR



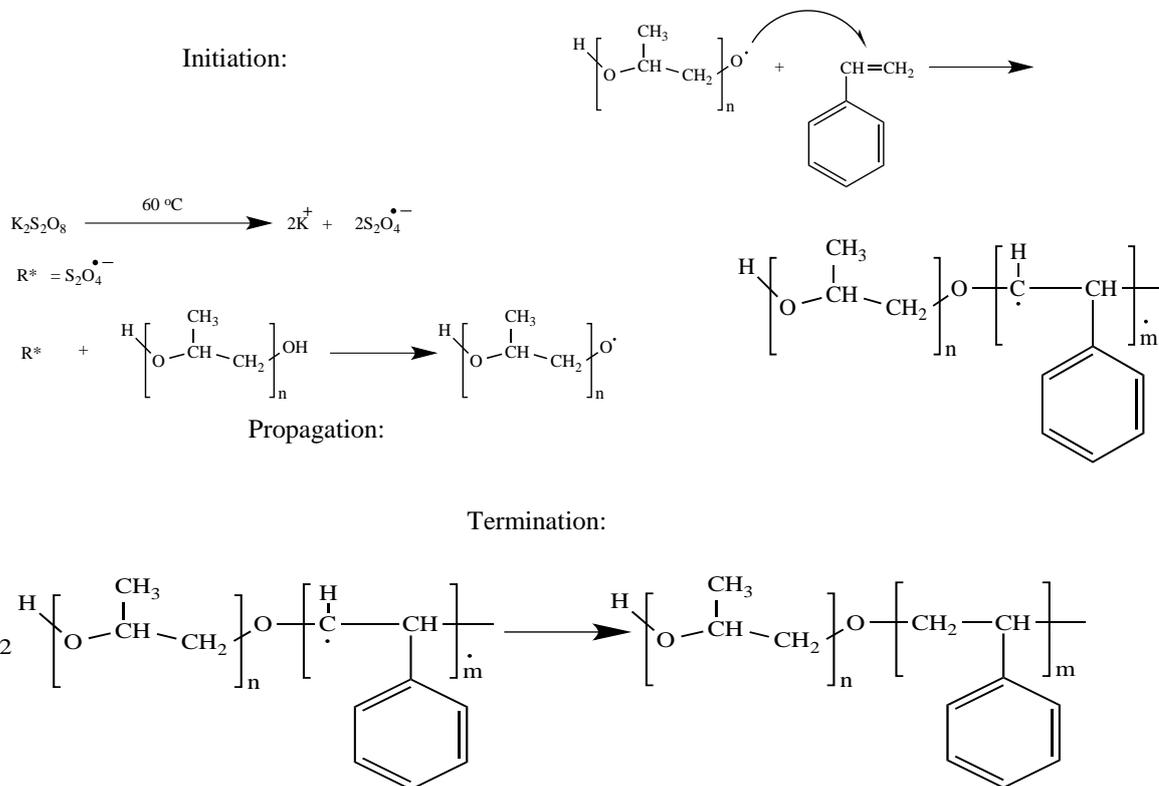
Scheme 3. Crosslinking of UPR in presence of styrene monomer.

Results and discussion

Grafted copolymer's structure

FT-IR spectra of the PPG is shown in Figure 1a. Absorption peak at 3400 cm^{-1} due to the stretch OH group, peak at 3000 cm^{-1} for stretch C – H and 1100 cm^{-1} is ascribed to O – C group. Figure 1b presents the FTIR spectrum of grafted copolymer

PPG-graft-St.). The results showed new peaks at 1500 cm^{-1} and 2900 cm^{-1} correspond to (C = C) and (C-H) aromatic. Peak at 1036 cm^{-1} which is attributed to stretch vibrations of C – O – C and confirm the point of grafting St unto PPG. Furthermore, the transmittance of the hydroxy group reduced more than 75% due to the grafting polymerization process as shown in Scheme 4.



Scheme 4: Mechanism of grafted St onto PPG.

Viscosity

Figure 2a-c. shows the viscosity of UPR mixed with different concentrations of grafted copolymers at various composition ratios (samples M1, M2 and M3) to investigate the state of UPR related to flow character at different speeds (rpm). The results showed that the viscosity of UPR decreased with increasing the spindle speed from 5 rpm to 50 rpm at $20\text{ }^\circ\text{C}$, as shown in Figures 2a-c. Furthermore, as the concentration of grafted copolymers increases from 0.1 to 0.5 gm, the viscosities increase. For example, the sample containing 0.1 gm of the prepared copolymer (M1) had viscosity 631 mPas at 5 rpm and 501 mPas at 50 rpm, while 0.5 gm (M1) gave 691 mPas at 5 rpm and 637 mPas at 50 rpm. In addition, the values of viscosity for UPR mixed with grafted copolymer increased with increasing the ratio of styrene in the copolymer. The value of viscosity of UPR combined with M3 is higher than those of M1 and M2, respectively. 0.5 gm (M3) gave the highest

viscosity (818 and 691 mPas) at 5 and 50 rpm, while 0.5 gm (M1) gave the lowest viscosity (691 and 637 mPas) at 5 and 50 rpm, respectively. The increased viscosity of UPR with increasing styrene ration in the copolymer is due to the effect of the copolymer chain on the orientation of the UPR in the flow direction and deformation of the chains [16].

Thixotropic index (TI)

Viscosity and thixotropic index are used to describe the rheology of the UPR. The effect of the concentration of grafted copolymer on the thixotropic index is shown in Figure 3. As clearly seen, the thixotropic index of UPR increased with increasing the ratio of styrene in the copolymer. This is attributed to the benzyl group in the grafted copolymer [17]. However, 0.1 gm of M1, 0.3 gm of M2 and 0.4 of M3 gave the highest value of the thixotropic index, as shown in Figure 3. The addition of grafted copolymer improved the thixotropic index of UPR

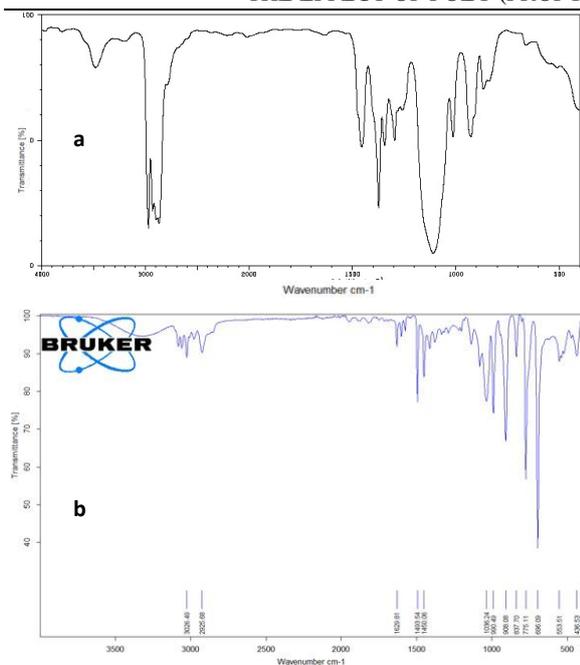


Fig. 1. FTIR spectra of (a) PPG and (b) PPG – g – St copolymer.

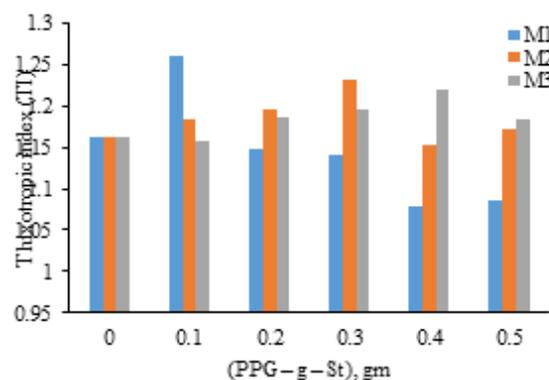


Figure 3. The effect of PPG – g – St copolymer composition and content on the thixotropic index of UPR.

Gel time and curing temperature

The period from the moment of adding the initiators to gelation is called the gelling time. In connection with the growth of polymer chains, the viscosity of the system increases, gelling occurs and is associated with the formation of a spatial molecular network, which leads to a loss of fluidity and loss of solubility. Figure 4 presents an increase in gel time of UPR with increasing the copolymer concentrations from 0.1 gm to 0.5 gm. However, as the styrene ratio increased from 15 to 35%, the gel time decreased from 10 minutes to 9 minutes at 0.5 gm. As can be seen that grafted copolymer based on PPG and St reduced gel time of UPR. These results confirm that the gel time of UPR depends on the composition of polymer and its concentration [18, 19].

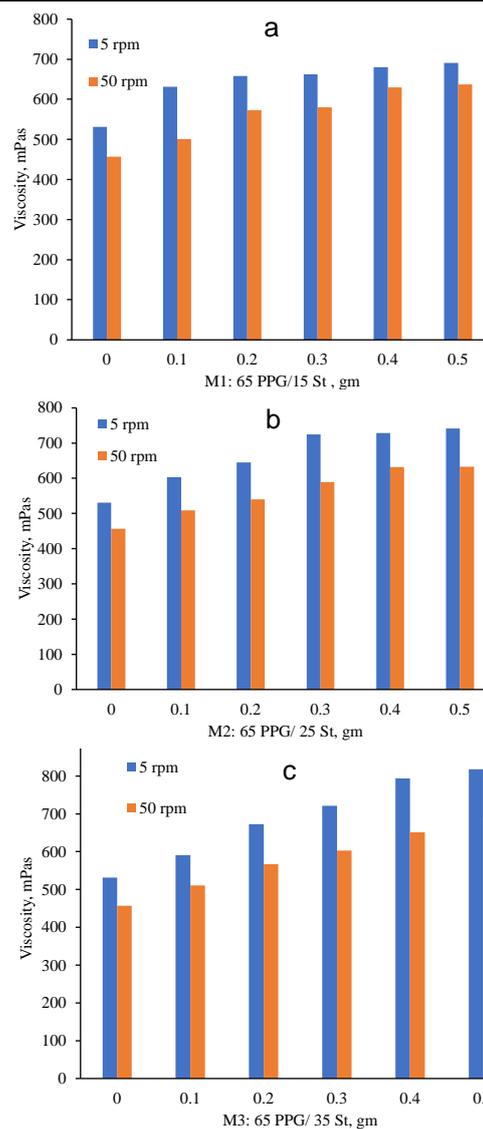


Fig. 2. The effect of PPG – g – St copolymer composition and content on the viscosity of UPR at different shear speed rates.

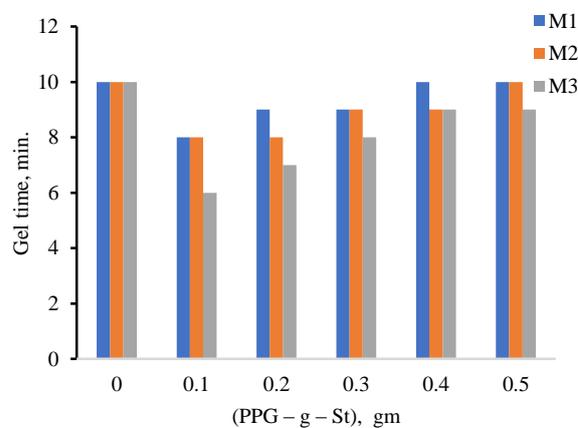


Fig. 4. The effect of PPG – g – St copolymer composition and content on gel time of UPR.

The amount of grafted copolymer to reach the maximum temperature (T_{max} , °C) for the UPR is shown in Figure 5. The addition of copolymer to UPR increased the temperature peak to 181 °C for M1, from 170 °C to 182 °C for M2 and 170 °C to 183 °C for M3 with increasing the concentrations of the copolymer from 0.1 gm to 0.5 gm.

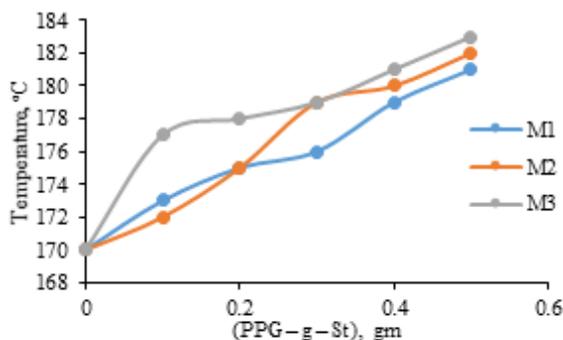


Fig. 5. The exothermic cure temperature of UPR as a function of copolymer (PPG - g - St) content.

Hardness

Figure 6 depicts the hardness of modified UPR cured films in terms of different concentrations of the copolymer and different ratios of styrene. The results showed that hardness increased with increasing concentrations of the copolymer from 0.1 to 0.5 gm. Also, as the ratio of styrene increases, the hardness of UPR cured films increased. This is attributed to the presence of benzene ring in the copolymer chain, which increases rigidity and hardness [20, 21]. 0.5 gm of M3 (35% St) gave the highest hardness 53, while 0.5 gm of M1 (15% St) gave hardness 48 (Shore D).

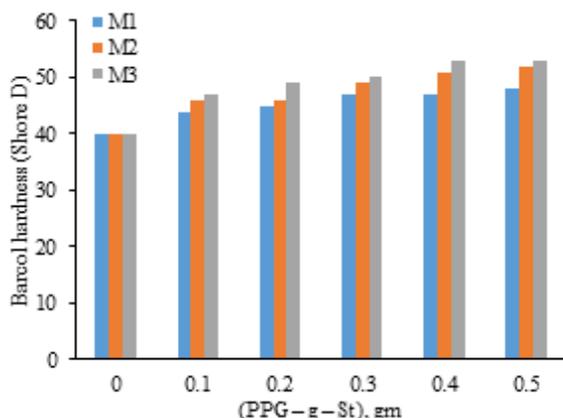


Fig. 6. the effect of PPG - g - St copolymer composition and content on the hardness of UPR.

Tensile strength

Figure 7 shows that the tensile strength increased with increasing the ratio of St in the copolymer backbone. For example, the tensile strength of M3 (35% St) is 154 MPa, and this drops down to 147 (M2, 25% St) and 142 MPa for M1 (15% St) at concentration 5 gm. This is due to the increased (St) content in the grafting copolymer. However, the tensile strength of UPR films increases with increasing the concentration of grafted copolymers.

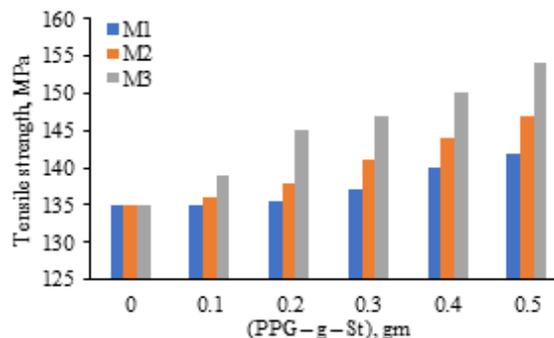


Fig. 7. The effect of PPG - g - St copolymer composition and content on the tensile strength of UPR.

Water uptake

The effect of copolymer grafted with different concentrations and ratio of St on the water uptake percentage of UPR cured films up to 50 days is shown in Figure 8. Water uptake percentage decreased with increasing the concentration of grafted copolymer and increasing St ratio in the copolymer. However, the minimum uptake water percentage (0.08%) was noticed with copolymer grafted of St ratio 35% followed by copolymer of St 25% (0.11%) and St 15% (0.17%) at concentration 5 gm compared to the control.

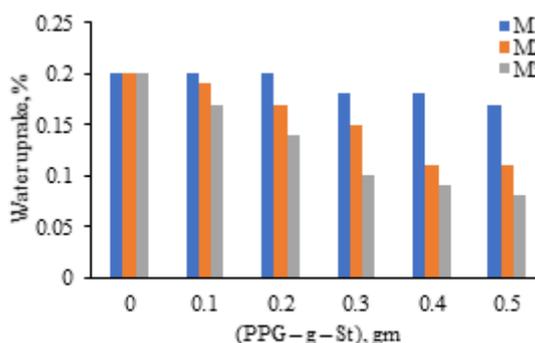


Fig. 8. The effect of PPG - g - St copolymer composition and content on the water uptake percentage of UPR.

Compressive strength

The compressive strength of UPR mixed with grafted copolymers is illustrated in Figure 9. It is clear that the compressive strength of UPR films increases as the St ratio increased in copolymer grafted. However, the compressive strength of UPR films increased with increasing the concentrations of copolymer grafted in UPR films. Based on Figure 9, it was observed that UPR films that containing copolymer with ratio (M3: 65 PPG/35 St) showed the highest strength (49.5 MPa), while UPR containing copolymer grafted with ratio (M1: 65 PPG/ 15 St) showed the lowest compressive strength (35 MPa) at concentration 5 gm. The increase in compressive strength is due to the low viscosity of UPR, high tensile strength and hardness. Generally, the compressive strength of UPR is affected by the physicomechanical properties of polymers, including tensile strength and hardness [22, 23].

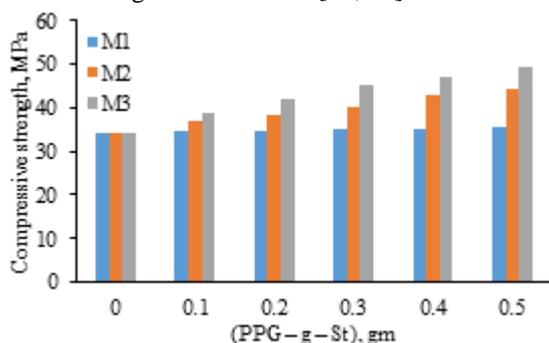


Fig. 9. The effect of PPG – g – St copolymer composition and content on the compressive strength of UPR.

Chemical resistance

The chemical resistance of UPR films was given in Table 2. The obtained results indicated that UPR films based on copolymer grafted were not affect when immersed in acid and alkali solutions. UPR films had had chemical resistance to acid and alkaline as shown in Table 2.

Table 2: Chemical properties of pure UPR and UPR mixed with the grafted copolymer.

Chemical solvent	UPR	UPR + M1	UPR + M2	UPR + M3
Nitric acid (10%)	o	o	o	o
Phosphoric acid (10%)	o	o	o	o
Sulfuric acid (10%)	o	o	o	o
Sulfuric acid (30%)	o	o	o	o
Acetic acid (10%)	o	o	o	o
Acetic acid (30%)	o	o	o	o
Ammonia (10%)	o	o	o	o
Ammonia (30%)	o	o	o	o
o	Pass			

Conclusions

The properties of UPR premixed with PPG – g – St copolymer were investigated. The grafted copolymers were based on propylene glycol and different ratio of St. The results showed that the viscosity, maximum temperature, hardness, tensile strength, and compressive strength increase with an increased St ratio in the grafted copolymer and concentration of grafted copolymer due to the increasing rigidity of styrene in the mixes of UPR. Thixotropic index and gel time decrease with increasing St ratio in the grafted copolymer. However, 0.1 gm of 65 PPG/15 St, 0.3 gm of 65 PPG/25 St and 0.4 gm of 65 PPG/35 St gave the highest thixotropic index.

Conflicts of interest

There are no conflicts to declare

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References

1. Waigaonkar S, Babu B, Rajput A., Curing Studies of Unsaturated Polyester Resin Used in FRP Products. *Jaico*: India 123 (2011).
2. Hassen H, Khazaal M, Majeed N, Hassan E., Preparation and identification of aromatic copolyester containing chalcone groups. *Egyptian Journal of Chemistry* 64(8): 4173-4181 (2021).
3. Jonhson K, Yang L., Preparation, Properties and Applications of Unsaturated Polyesters in Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters. J. Scheirs and T. Long, Eds. West Sussex, UK: John Wiley & Sons, Inc., 699–712 (2003).
4. Andjelkovic D, Culkin D, Loza R., Unsaturated Polyester Resins Derived from Renewable Resources. *Composites & Polycon* 1–6 (2009).
5. Thakur VK, Thakur MK, Pappu A., Hybrid Polymer Composite Materials, Woodhead Publishing Limited, Cambridge, UK, (2017).
6. Li XQ., The research progress of unsaturated polyester resin for coatings in

- China. *Shanghai Coatings* **49**(12), 36–39 (2011).
7. Schuller A.-S., Delaite C, Farge H., Effect of a formulation named “giral” on mechanical properties of a composite based on silica and unsaturated polyester resin. *Polym. Bull.* **66** (1), 77–94 (2011).
 8. Grea SA, Ghebaur A, Constantin F, Iovu H., New hybrid materials based on modified halloysite and unsaturated polyester resin. *Polym.- Plast. Technol.* **50** (11), 1096–1102 (2011).
 9. Grea SA, Iovu H, Bulearca A, New organophilic agents of montmorillonite used as reinforcing agent in epoxy nanocomposites. *Polym. Test.* **27**(1), 100–113 (2008).
 10. Mariusz O, Maciej H, Henryk G., Thixotropic compositions: unsaturated polyester resins/modified bentonites. *Polimery* **52**(5) 345-350 (2007).
 11. Lisyukov DO, El-Sayed Negim, Efremov SA, Nechipurenko SV, Irmukhametova GS., producing sustainable unsaturated polyester for fiberglass application. *AIP Conference Proceedings* **2124**(1), 030011-4, (2019).
 12. Lisyukov DO, El-Sayed Negim, Efremov SA, Nechipurenko SV, Irmukhametova GS., Unsaturated polyester resin based on glycolysis of polyethylene terephthalate. *Patent. Kazakhstan* No. 2019/ 1048
 13. Diana K, Volodymyr L, Ulyana K, Volodymyr M, Andrii M., Physicochemical Principles of Synthesis and Modification of Unsaturated Polyester-Polyvinyl Chloride Composites and the Properties of Materials Derived from Them. *International Journal of Polymer Science*, 1-9 (2019).
 14. Benny AC, Beena TA, Thomas ET., Modification of unsaturated polyester resin by polyurethane prepolymers. *Journal of Applied Polymer Science* **100**(1), 449-456 (2006).
 15. El-Sayed Negim, Konysbay AM, Irmukhametov GS, Kalugin SN., Synthesis and characterization of polypropylene glycol-graft-styrene. *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a. = Complex Use of Mineral Resources = Mineraldik Shikisattardy Keshendi Paidalanu.* **3**(318), 5-11 (2021).
 16. Ayoub MMH, El-Awady MM, Nasr HE, **Negim SM.**, Synthesis and Rheological Properties of Some Styrene/Methacrylate Copolymer Lattices. *J. Polymer-Plastics Technology and Engineering* **42**(5), 863-881 (2003).
 17. Oleksy M, Heneczowski M, Galina H., Thixotropic compositions: unsaturated polyester resins/ modified bentonites. *Polimery* **52**, 345-350 (2007).
 18. Huang YJ, Su CC., Effects of poly(vinyl acetate) and poly(methyl methacrylate) low-profile additives on the curing of unsaturated polyester resins: Rheokinetics and morphological changes up to gelation. *Polymer* **35**, 2397- 2410 (1994).
 19. Mohamad HB, Mehran H, Mehdy V., Evaluation of Low-profile Additives in the Curing of Unsaturated Polyester Resins at Low Temperatures. *Iranian Polymer Journal* **15**(2), 143-153 (2006).
 20. Mallakpour S, Rafiee Z., Step-growth polymerization of 5-(3-Acetoxyphenylamino) isophthalic acid with different aromatic diols. *Iran Polym. J.* **17**, 217-226 (2008).
 21. Yeo JS, Lee JH, Hwang SH., Effects of lignin on the volume shrinkage and mechanical properties of a styrene/unsaturated polyester/lignin ternary composite system. *Composites Part B: Engineering* **130**(1), 167– 173 (2017).
 22. Peutzfeldt A, Asmussen E., The effect of postcuring on quantity of remaining double bonds, mechanical properties, and in vitro wear of two resin composites. *Journal of Dentistry* **28**, 447-452 (2000).
 23. Cesar PF, Miranda WG, Braga RR., Influence of shade and storage time on the flexural strength, flexural modulus, and hardness of composites used for indirect restorations. *Journal of Prosthetic Dentistry* **86**, 289-296 (2001).