Toughening of unsaturated polyester resin by solid elastomers and liquid rubbers: A review

Chandresh M. P., Ani Dechamma C. D., Bhavana M., Rameshwara N., Roopa S.

Department of Polymer Science and Technology, Sri Jayachamarajendra College of Engineering, JSS Science and Technology University, Mysuru 570006, Karnataka, India.

---***---

Abstract - *Unsaturated polyester (USP) resins are thermosetting polymers that have been known for many years for its thermal and chemical resistance. They are widely used matrices for composite applications. However, their low toughness makes them limited for the applications where toughness becomes a critical property. Thus, these resins need to be modified by toughening agents (tougheners) to improve their fracture toughness or increase their impact resistance. In order to improve the toughness of USP resins, researchers have used different material incorporations viz. elastomers, thermoplastics, and particulate / fibrous fillers into the USP matrix. The intent of this paper is to review the varied research that has been performed to improve the toughness of USP resin by elastomer modification. This review summarizes the effect of various elastomers (both solid elastomers and liquid rubbers) on the toughness of the USP resin. It also covers the chemical modifications employed with those elastomeric tougheners, and the additional incorporation of certain fillers, which have resulted in much higher toughness along with combating other property reduction due to softer elastomeric inclusions.*

Key Words: Unsaturated polyester resin, liquid rubber, toughness, impact resistance, elastomer, USP, UPR.

1. INTRODUCTION

Unsaturated Polyester (USP) is a versatile and low-cost condensation resin formed generally by the reaction of polyols (also called polyhydric alcohols) with unsaturated dibasic acids whose production started in the year 1930 [1]. These resins are generally pale-yellow oligomers with a low degree of polymerization and are viscous liquids depending on their chemical composition and molecular weight (100–3000 g/mol) [2]. USP resins are one among the many thermo-setting resins and belong to family of esters [Figure 1]. They have excellent corrosion resistance, chemical resistance, fire resistance, rapid crosslinking, dimensional stability, design flexibility and processing properties. They find application in sanitary wares, tanks, pipes, gratings and high-performance components for marine and transportation industry (closure, body panels, fenders, boat hulls, decks etc.) [3]. Unfortunately, USP resins are brittle just like other thermo setting resins viz. epoxy, phenolics and vinyl esters. So, un-modified USP resins are not preferred in the applications like construction and transportation due to its low impact strength, low elongation at break and poor

resistance to crack propagation. Thus, their application is limited as polymer matrix in the fibre or filler reinforced composite products. Hence, there is a need for toughening the USP resin to increase its scope of applications.

2. CLASSIFICATION

USP resins can be classified based on the type of starting materials that are used for its synthesis (having different structure or chemical family). In general, it can be aliphatic USP resin or aromatic USP resin. The former being easily processible and latter being developed for the high-performance applications. USP resin is also classified based on the chemical groups present as given in Table 1. These resins are developed to tune the properties as per the end use requirements [4].

Table -1: Classification of USP resin based on chemical group

Classification/ Type of USP resin	Remarks
Phthalic acid type (Ortho resins)	- General-purpose resins - Based on anhydrides or acids and glycols 35%-45% of styrene content - Styrene group reduces flexibility in the backbone with reduced thermal resistance
Isophthalic acid type (Iso resins)	- General-purpose resins - Derived from anhydrides or acids and glycols 42%-50% of styrene content - High viscosities, better thermal and chemical resistance - The cured Iso resins have high T_g - Too brittle for many engineering applications in the absence of reinforcements
Bisphenol-A type (bisphenol-A fumarates)	- Derived from glycol or oxide diether of bisphenol-A and fumaric acid - High degree of hardness and rigidity - Better thermal resistance

Halogenated USP resin	• Synthesized by halogen (Cl/Br) containing anhydrides or phenols • Provide flame resistance
Vinyl ester resin (ethylene - based ester type)	• Produced by esterification of epoxy with acrylic or methacrylic acid • 35% - 45% of styrene content • Strength and bulk cost are intermediate between polyester and epoxy • Used as an alternative for conventional epoxy [2, 4]

3. SYNTHESIS

USP resin is synthesized by esterification reaction of unsaturated dibasic acids or anhydrides with dihydric alcohols. Wide variety of grades are possible by using different kinds of starting materials [5]. USP resins are produced via batch process in cylindrical reactors equipped with stirrer, condenser and a jacket heater. This makes their synthesis both at laboratory and industry very similar.

The reactor is filled with glycol at room temperature in slight excess (5%) in order to compensate the losses during condensation because of volatility and side reactions. Then, maleic anhydride and phthalic anhydride are charged into the reactor. Typically, for a general-purpose unsaturated polyester resin, the ratio is 1 mol maleic anhydride, 1 mol phthalic anhydride, and 1.1 mol of 1,2-propylene glycol. Once the raw materials are added the reactor is purged with nitrogen to avoid discoloration, and slowly heated at 90 ^{0}C which initiates exothermic reaction between anhydrides and glycol followed by elimination of water as by-product. The rate of reaction is influenced by structure and stoichiometry of the glycol and dibasic acid components. Two main reactions involved in this synthesis are: (a) monoester formation and (b) polycondensation. The monoester forms at a temperature range of 60–130 ^{0}C, while the polycondensation takes place above 160 ^{0}C. The by-product has to be removed continuously, since it is a reversible reaction. The formation of polyester resin is controlled by the measurement of acid value and viscosity. The molecular weight of USP resin would be about 3000 g/mol or less at equilibrium. Further, increase in polycondensation leads to gel formation. Several new approaches have been made to increase M_n to 5000 g/mol, as that, such resins on curing, give networks with better toughness and mechanical strength [2, 6]. Also, to have the tailor-made properties in the USP resin, keeping the reaction mechanism same, the starting materials are varied. For example, instead of using only simple monomers, a long chain monomer or pre-polymer or telechelic polymer or combination of such multiple starting materials are employed. This results in varying the degree of chain flexibility and unsaturation.

4. CURING

As the USP resins are low molecular weight resins, they need to be crosslinked to form a rigid solid. Unlike the other thermosets viz. epoxy, urea formaldehyde (UF), melamine formaldehyde (MF), phenol formaldehyde (PF) which cures using the reactive functional groups present in them; the USP resin cures using the unsaturation (pi bonds) present in them to result in three-dimensional network. USP resin is an easily printable liquid polymer, which is usually crosslinked using curing agents; and once cured, it keeps the solid shape formed inside the mould. Some USP resins, could consist of two distinct segments (a short chain polyester containing double bonds and a vinyl repeating unit) and the curing may be slightly complex, in the sense that, either the temperature or the curing agents that are required to crosslink both these segments of USP resin may vary and it needs to be handled carefully.
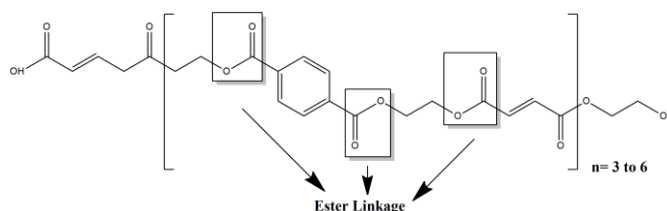

Figure -1: Representative/ Indicative USP resin showing the ester linkage

Peroxides, diacyl peroxides, peresters, perketals, ketones, dialkyl peroxides and hydro peroxides are commonly used catalysts or hardeners for curing unsaturated polyester resin. Among various curing reactions, the cross-linking of USP resin with styrene (30-40% by mass) is widely used [Figure 2]. It is carried out along with the use of organic peroxide as catalysts at elevated temperature and cobalt salts as accelerator. USP resin can be cured both at room temperature and at elevated temperatures 149-163 ^{0}C based on the nature of curing system used.
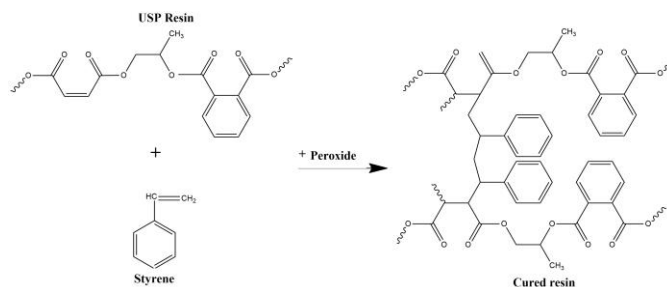

Figure -2: Scheme of curing of USP resin

The addition of an organic peroxide is sufficient to cure above 82 ^{0}C, but curing at lower temperatures requires the use of both a peroxide catalyst (benzoyl peroxide, cumene hydroperoxide, di-tert-butyl peroxide and methyl ethyl ketone peroxide (MEKP)) and a promoter (organic cobalt salts and dimethyl- or diethyl- aniline). The control of gelation and cure is the most critical part of polyester resin technology. It is extremely difficult to arrest the cross-linking

reaction at the gel stage. Gelation is followed immediately by a self-propagated cure with considerable evolution of heat. USP resin molecules before curing are short chain of molecules (molar mass generally 100 to 3000 g/mol) which once cross-linked form a huge mesh structure [7-9].

5. BRITTLENESS

USP resins are highly cross linkable or thermosetting polymers that are developed using short chain molecules. USP resin is amorphous thermosetting substance with a T_g of 80 °C upon curing. As the Tg of USP resin is higher compared to elastomers, they are hard and brittle at room temperature. Thus, the combination of higher T_g and the cross-linked structure of USP resins makes them to be brittle and possess poor crack growth resistance [10, 11]. The high degree of molecular crosslinking results in number of superior properties (viz. high glass transition temperature, high modulus, specific strength, high creep resistance, good dimensional stability at elevated temperature, and good solvent resistance). Unfortunately, even the brittleness with poor resistance to crack initiation and propagation (Brittle fracture) is also resultant of the same [Figure 3]. This lack of toughness severely impacts the performance of highly cross-linked thermosets like USP resin [7]. Toughness of material is the combination of its strength (ability to withstand the load) and ductility (elongation while breaking under that load). This brittle failing nature of USP resin is not acceptable where a high degree of safety is essential.
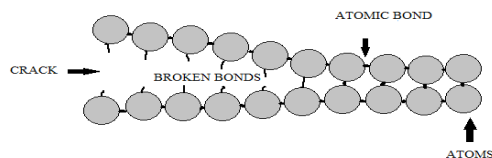

Figure-3: Representation of Brittle Fracture

6. TOUGHENING OF USP RESIN

As USP resin is used in many commercial and crucial applications, many researchers have found ways to improve its fracture toughness to impart safety of the products during service. So, in order to toughen USP resin, several types of tougheners are employed including high molecular weight polymers (engineering thermoplastics and solid elastomers); low molecular weight polymers (oligomers or liquid rubbers); micro / nano fillers which includes graphene oxide-derivatives, clay nano composites, halloysite nanotubes/silica nano hybrid, boron-nitride nanosheets; some liquids like tung oil. Among them, the toughness enhancement caused by solid elastomers and liquid rubbers are discussed in this section, and the same has been compiled in the Table 2 [12-17].

In 2006, Pachpinyo et al., blended natural rubber latex (NRL) with USP resin in the presence of dispersion aids

(sodium lauryl sulfate (SLS), toluene, and ammonia) to improve the impact resistance of USP resin. They found that the cured samples had higher impact strength than pure USP resin regardless of the type of dispersion aid used. But, due to low elastic modulus of NRL, tensile strength and flexural strength of blended samples have been reduced [18]. In another study, Roy et al. used core–shell poly(siloxane)-epoxy microspheres to improve dynamic properties of USP resin. The addition of core–shell poly(siloxane)-epoxy microspheres decreased the tensile strength and modulus whereas, the impact strength was increased by 101 % [19]. Modest improvement in fracture toughness of the USP resin with the addition of amine terminated butadiene-acrylonitrile (ATBN) rubber was observed by Miller and Stirling [20]. This was attributed to the formation of large agglomerates of mixture of the rubber and the base resin rather than forming a discrete droplet. When glass fiber was reinforced with this, it resulted in increased fracture toughness due to combination of localized bonding between rubber/resin agglomerates and the glass fibers but it lowered the tensile strength and flexural modulus of resin.

In addition to toughness modifications with solid elastomers, Maleimido-terminated liquid acrylonitrile butadiene rubber (mt-LNBR) was blended with USP resin. This led to improved fracture toughness compared to the unmodified LNBR due to chemical interactions, which was also confirmed by the localized shear yielding as per SEM micrographs studied by Abbate et al., however, flexural modulus and yield stress were reduced [21]. Ullett and Chartoff [22], separately blended USP resin with carboxy terminated LNBR (ct-LNBR), vinyl terminated LNBR (vt-LNBR), epoxy terminated LNBR (et-LNBR), hydroxy terminated poly ether (of epichlorohydrin) (HTE), poly ethyl hexyl acrylate (EHA), and poly butyl acrylate (BA) between 1 – 4.6 pph. They observed that, toughness was increased with reduction in modulus. USP resin was toughened by incorporating novel liquid polyurethane rubber (LPUR). Fracture toughness of USP resin was increased 1.9 times with the formation of cavitated particles. Hence, in order to increase the fracture toughness of rubber-modified USP, more cavitated (i.e., smaller) rubber particles are necessary. The toughness of highly cross-linked USP resin can be increased without decreasing the cross-link density by incorporating well-bonded small particles with balancing the particle size, the volume fraction, and the properties of the rubber [23]. Blend of USP resin and polybutadiene rubber (PBD) was developed by Ragosta et al., [24] and was compatibilized using the copolymer of PBD and USP. Fracture measurements performed on the cured samples showed a significant increase in toughness in the presence of copolymer (that is, compatibilizing agent). The fracture strength was increased by increasing the content of the copolymer. The presence of this compatibilizing agent helped in reduction of the size of the rubber particles due to superior interface bond and this resulted in increment of confined shear yielding in the USP resin grid around the rubber particles.

Table – 2: Effect of various rubbery impact modifiers on toughness of USP resin

Impact modifier	Quantity	Effect on Impact Properties	Effect on other properties	Testing Standard [a]	Reference
Natural rubber latex (NRL)	10, 15, 20, 25 phr	Improved Impact strength with 15phr NRL	Tensile and flexural strength reduced.	ASTM D356-93A and ASTM D638	18
Core–shell poly siloxane-epoxy microsphere	3–10 wt%	Impact strength and fracture energy increased	Tensile strength and modulus reduced.	ASTM D638 and ASTM D 256	19
ATBN	5, 10 and 15 wt%	Improved fracture toughness	---	ASTM D5045	20
ITBN and ATBN	4, 8, 10, 15 wt%	ITBN showed higher toughness with USP resin compared to ATBN	Brittleness and Dynamic storage modulus reduced.	---	21
CTBN, VTBNX, ETBNX, HTE, EHA, BA	0.05-2 wt%	Improved toughness	T_g and storage modulus reduced	ASTM D638	22
LPUR	3-32 vol%	Improved fracture toughness	T_g reduced	ASTM E-399	23
PBD	4, 8, 10, 15 wt%	Improved fracture toughness	---	---	24
LNR and LENR	1.5, 3, 4.5 and 6 wt%	LENR modified USP exhibited higher impact strength	Tensile modulus decreased.	ASTM D4812 and ASTM D-638	25
CTBN	5, 10, 15 phr	Maximum toughness at 15 phr CTBN	---	---	26
ATBN	5, 10 and 15 wt%	Improved fracture toughness	---	ASTM D5045	27
Hycar, ct-LNBR & vt-LNBR	2.5, 5, 10, 15, 20, 30 wt %	Increased Fracture toughness of USP by about 62%	Young's Modulus decreased.	---	28
LENR	1.5, 3 and 4.5 wt %	Improved toughness and impact energy	stiffness, yield strength & thermal resistance reduced	ASTM D4812	29
LNR	1.5, 3, 4.5 wt%	Improved impact resistance due to CNC & STNC	Modulus, tensile strength and T_g reduced.	ASTM D-638	30

[a] The testing standards pertain to following property measurement:
ASTM D5045 – Plain strain fracture toughness and strain energy release rate
ASTM D638 – Tensile properties
ASTM E-399 – Plain strain fracture toughness
ASTM D4812 – Impact resistance
ASTM D356-93A – Impact strength
ASTM D 256 – Impact resistance

Further, USP resin was modified by two different reactive rubbers, liquid natural rubber (LNR) and liquid epoxidized natural rubber (LENR). Both the rubber-modified resins improved tensile strength. A slight decrease in the glass transition temperature (T_g) of the USP resin was accounted on the addition of the liquid rubbers. The impact strength and fracture toughness were increased at 1.5 wt % for LNR and 4.5 wt % for LENR-modified USP resin. Both LNR and LENR improved the mechanical properties (viz. tensile strength, fracture toughness and impact strength) of USP resin. LENR/USP resin demonstrated better mechanical performance compared to the LNR/USP resin [25]. Carboxy-terminated acrylonitrile-butadiene copolymer (CTBN) was introduced into USP resin matrix along with epoxy-terminated triblock copolymer (ETBN) as compatibilizer which reduced the interfacial tension between the components and in-turn modifying the morphology by decreasing the particle. This resulted in enhanced impact behaviour reducing failures generated by the presence of large particles [26]. Addition of ATBN rubber to brittle USP resin resulted in notable improvement of fracture toughness. With the additional reinforcement of glass fibre (GF) to this mixture, showed an improved transverse cracking strain [27].

Maspoch et al., [28] studied the effect of vinyl terminated LNBR (vt-LNBR), polyester thermo plastic elastomer (polyester TPE) and modified PMMA on toughness of USP. It was noticed that, vt-LNBR offered better toughness than polyester TPE and modified PMMA. The toughness was increased by 62% after the incorporation of vt-LNBR.

USP was investigated upon incorporating modified liquid epoxidized natural rubber (LENR) along with CNC. The LENR content improved the toughness of USP resin, but decreased the stiffness, yield strength, thermal resistance and modulus [29]. In 2015, by Kargarzadeh et al., [30] LNR toughened USP resin was reinforced with cellulose nanocrystal (CNC) derived from kenaf blast fibres. Both untreated CNC and silane treated CNC (STCNC) were mixed with USP resin/LNR blend to study the morphological, tensile and thermal properties of the resulting composites. The results showed that tensile modulus increased with both kind of CNC whereas, untreated CNC-LNR-USP resin composites were stronger. It was also found that impact resistance of USP resin increased with increase in LNR and CNC content.

7. SUMMARY

Based on the above research findings, it can be summarized that, the addition of an elastomeric additive (solid elastomers or liquid rubbers) as tougheners was found to be the widely accepted and frequently used method to improve the toughness of brittle thermosets. However, the rubbery tougheners tend to reduce the strength and T_g. So, in-order to control its reduction, the functionalization approach of tougheners was adapted. Which imparted stronger interaction between the USP resin and rubbery phase. An

additional incorporation of reinforcing 'micro or nano' fillers were even more effective.

Also, the extent of toughness improvement depends not only on the type of tougheners, its chemical modifications, or the filler incorporation, but also depends on the process of blending and curing. Because, it results in development of various phase morphologies of the USP resin compound due to the variations in the conditions used. For example, the separation of rubber as a discrete second phase during curing, is known to greatly improve the fracture toughness. But this morphology is well attained provided the second phase satisfies few conditions related to its size, shape, volume fraction, dispersion and adhesion. Thus, the overall morphology also significantly affects the fracture toughness of the final material.

REFERENCES

[1] P. Penczek, P. Czub, and J. Pielichowski, "Unsaturated polyester resins: Chemistry and technology," in Crosslinking in Materials Science., Berlin, Heidelberg: Springer Berlin Heidelberg, Jul. 2005, pp. 1–95, doi:10.1007/b136243.

[2] M. Malik, V. Choudhary and I. K. Varma, "Current status of unsaturated polyester resins," Journal of Macromolecular Science, Part C: Polymer Reviews, vol. 40, 2000, pp. 139–165, doi:10.1081/MC-100100582.

[3] J. E. Sayre and P. A. Elias, "Unsaturated Polyesters: Their Uses Range from Baby Cradles to Coffins; Boats Is a Fast-Growing Market for the Reinforced Unsaturates," Chem. Eng. News, vol. 37, 1959, pp. 56–62.

[4] Sushil, "Unsaturated polyester resin introduction, properties and classification," Frptitan.com., 07-Apr-2018. [Online]. Available: https://frptitan.com/625-2/. [Accessed: 24-Mar-2021].

[5] A. Benny Cherian and E. T. Thachil, "Toughening studies of an unsaturated polyester resin using maleated elastomers," Prog. Rubber Plast. Technol, vol. 17, Dec. 2001, pp. 205–224, doi:10.1177/147776060101700401.

[6] J. K. Fink, "Unsaturated Polyester Resins," Reactive Polymers Fundamentals and Applications., Elsevier, 2005, pp. 1–67, doi:10.1016/b978-081551515-9.50003-2.

[7] R. P. Singh, M. Zhang and D. Chan, "Toughening of a brittle thermosetting polymer: effects of reinforcement particle size and volume fraction," Journal of materials science, vol. 37, 2002, pp. 781–788, doi:10.1023/a:1013844015493.

[8] "Polyester Resins," Scribd.com. [Online]. Available: https://www.scribd.com/document/397740688/Polyester-Resins. [Accessed: 24-Mar-2021].

[9] A. Steyermark, "Kirk-Othmer encyclopedia of chemical technology, vol. 1, 3rd ed," Microchem. J, vol. 24, 1979, p. 389, doi:10.1016/0026-265x (79)90018-3.

[10] B. Cherian and E. T. Thachil, "Elastomer toughening of isophthalic polyester resin," Polym. Plast. Technol. Eng, vol. 44, 2005, pp. 391–405, doi:10.1081/pte-200048275.

[11] M. L. L. Maspoch and A. B. Martinez, "Toughening of unsaturated polyester with rubber particles. Part I: Morphological study," Polym. Eng. Sci, vol. 38, Feb. 1998, pp. 282–289, doi:10.1002/pen.10189.

[12] S. He, N. D. Petkovich, K. Liu, Y. Qian, C. W. Macosko and A. Stein, "Unsaturated polyester resin toughening with very low loadings of GO derivatives," Polymer (Guildf.), vol. 110, 2017, pp. 149–157, doi:10.1016/j.polymer.2016.12.057

[13] M. T. Albdiry, B. F. Yousif and H. Ku, "Fracture Toughness and Toughening Mechanisms of Unsaturated Polyester-Based Clay Nanocomposites,", vol. 5, Jun. 2013, p. 10.

[14] P. A. Jeemol, S. Mathew and C. P. R. Nair, "Maleimide end- capped polyether telechelics as novel toughening agents for unsaturated polyester resin," J. Polym. Res, vol. 27, Jul. 2020, doi:10.1007/s10965-020-02197-z.

[15] L. Chengguo, W. Lei, Z. Cai, J. Chen, L. Hu, Y. Dai and Y. Zhou, "Use of tung oil as a reactive toughening agent in dicyclopentadiene-terminated unsaturated polyester resins," Ind. Crops Prod, vol. 49, May. 2013, pp. 412–418, doi:10.1016/j.indcrop.2013.05.023.

[16] C. Fukai, D. Zhang, Y. Hou, S. Qiu, J. Wang, W. Hu and L. Song, "Construction of hierarchical natural fabric surface structure based on two-dimensional boron nitride nanosheets and its application for preparing biobased toughened unsaturated polyester resin composites," ACS Appl. Mater. Interfaces, vol. 10, Oct. 2018, pp. 40168–40179, doi:10.1021/acsami.8b15355.

[17] L. Jing, B. Zhong, Z. Jia, D. Hu, Y. Ding, Y. Luo and D. Jia., "In-situ fabrication of halloysite nanotubes/silica nano hybrid and its application in unsaturated polyester resin," Appl. Surf. Sci, vol. 407, Feb. 2017, pp. 130–136, doi:10.1016/j.apsusc.2017.02.149.

[18] P. Pachpinyo, P. Lertprasertpong, S. Chuayjuljit, R. Sirisook and V. Pimpan, "Preliminary study on preparation of unsaturated polyester resin/natural rubber latex blends in the presence of dispersion aids," J. Appl. Polym. Sci, vol. 101, Jul. 2006, pp. 4238–4241, doi: 10.1002/app.22506.

[19] P. K. Roy, N. Iqbal, D. Kumar and C. Rajagopal, "Rubber toughening of unsaturated polyester with core–shell poly(siloxane)-epoxy microspheres," Polym. Bull. (Berl.), vol.

71, Jul. 2014, pp. 2733–2748, doi:10.1007/s00289-014-1217-z.

[20] N. A. Miller and C. D. Stirling, "Effects of ATBN Rubber Additions on the Fracture Toughness of Unsaturated Polyester Resin," Polym. Polym. Compos, vol. 9, 2001, pp. 31–36.

[21] M. Abbate, E. Martuscelli, P. Musto, G. Ragosta and M. Leonardi, "A novel reactive liquid rubber with maleimide end groups for the toughening of unsaturated polyester resins," J. Appl. Polym. Sci, vol. 62, 1996, pp. 2107–2119, doi:10.1002/(sici)1097-4628(19961219)62:12<2107::aid-app13>3.0.co;2-2.

[22] J. S. Ullett and R. P. Chartoff, "Toughening of unsaturated polyester and vinyl ester resins with liquid rubbers," Polym. Eng. Sci, vol. 35, 1995, pp. 1086–1097, doi:10.1002/pen.760351304.

[23] S. Kim, K. Cho, J. H. An and C. E. Park, "Toughening mechanisms of modified unsaturated polyester with novel liquid Polyurethane rubber," J. Mater. Sci, vol. 29, 1994, pp. 1854–1866, doi:10.1007/bf00351305.

[24] G. Ragosta, M. Bombace, E. Martuscelli, P. Musto, P. Russo and G. Scarinzi, "A novel compatibilizer for the toughening of unsaturated polyester resins," Journal of materials science, vol. 34, 1999, pp. 1037–1044.

[25] Kargarzadeh, Hanieh, I. Ahmad, I. Abdullah, R. Thomas, A. Dufresne, S. Thomas and A. Hassan, "Functionalized liquid natural rubber and liquid epoxidized natural rubber: A promising green toughening agent for polyester," J. Appl. Polym. Sci, vol. 132, Jul. 2014, doi:10.1002/app.41292.

[26] L. Suspene, J.-F. Gerard and J.-P. Pascault, "Morphology of unsaturated polyester resin-additive blends," Polym. Eng. Sci, vol. 30, Dec. 1990, pp. 1585–1590, doi:10.1002/pen.760302405.

[27] B. A. Sjögren and L. A. Berglund, "Toughening Mechanisms in Rubber-Modified Glass Fiber/Unsaturated Polyester Composites: Toughening Mechanisms in GF/UP Composites," Polym. Compos, vol. 20, 1999, pp. 705–712.

[28] M. L. L. Maspoch and A. B. Martinez, "Toughening of unsaturated polyester with rubber particles. Part II: Fracture behavior," Polym. Eng. Sci, vol. 38, Feb. 1998, pp. 290–298, doi:10.1002/pen.10190.

[29] H. Kargarzadeh, R. M. Sheltami, I. Ahmad, I. Abdullah and A. Dufresne, "Toughened polyester cellulose nanocomposites: Effects of cellulose nanocrystals and liquid epoxidized natural rubber on morphology and mechanical properties," Ind. Crops Prod, vol. 72, Dec. 2014, pp. 125–132, doi:10.1016/j.indcrop.2014.12.052.

[30] H. Kargarzadeh, R. M. Sheltami, I. Ahmad, I. Abdullah and A. Dufresne, "Cellulose nanocrystal reinforced liquid natural rubber toughened unsaturated polyester: Effects of filler content and surface treatment on its morphological, thermal, mechanical, and viscoelastic properties," Polymer (Guildf.), vol. 71, Jun. 2015, pp. 51–59, doi:10.1016/j.polymer.2015.06.045.