RECYCLAMINE® - NOVEL AMINE BUILDING BLOCKS FOR A SUSTAINABLE WORLD

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ABSTRACT

Epoxy thermosets are high performance polymers having superior mechanical, adhesive, and very good chemical resistant properties, preferred for versatile applications in Composites, Coating, Construction, Electrical & Electronics segments. Unfortunately, unlike thermoplastics, thermosetting plastics are not recyclable. Thermoset waste generated during manufacturing and end-of-life pose significant ecological, environmental and societal challenges all over the world. A new class of high-performance amine-based epoxy curing agents, Recyclamines®, have been developed for the creation of inherently recyclable thermoset materials. Recyclamine® technology is based on specifically engineered recyclamine® curing agents which enables cleavage points that converts thermosetting epoxies into thermoplastics under specific set of conditions. These cleavage points are reversible at specific condition and hence enable disintegration of the thermoset matrix. During this disintegration process, all the valuable reinforcing components such as carbon fiber, glass fiber, kevlar®, plastic material in a thermoset composite, can be recovered. More importantly, the thermoset manufacturing waste can be recycled, reused and re-integrated back into the manufacturing ecosystem.

In this paper general overview of the recyclable epoxy technology and platform chemistry is presented, including the underlying chemical principle that fosters recycling and recovery of the cured thermoset epoxy. Recyclable epoxy systems based on Recyclamine® are developed and characterized for process and performance properties. Recycling and recovery of epoxy thermoset composite is demonstrated as proof of the concept.

INTRODUCTION

1.1 Background

The global epoxy thermoset market is valued at 2.7 million MT and estimated to grow at a CAGR of 5.5% for the next 8 years. Due to dense three dimension crosslinking, epoxy thermosets are conventionally non- recyclable which poses a challenge to dispose waste generated during the product manufacturing process of part or component at end of its service life. Specific to the composite industry in which epoxy resins are preferred matrix materials, the recycling of thermosets is becoming a compelling issue. Present methods for end of life disposal such as incineration, land filling and dumping into ocean cause severe concerns such as air pollution, ecological pollution , global warming, ground & ocean pollution.

According to world economic forum, by 2050 plastic waste will account for 12 billion MT and ocean will have more plastics than fishes. Thermal, Mechanical and Chemical recycling technologies (Figure 1) are often used to prevent the waste from entering landfill or a water body however these technologies have disadvantages and limitations including economic viability.

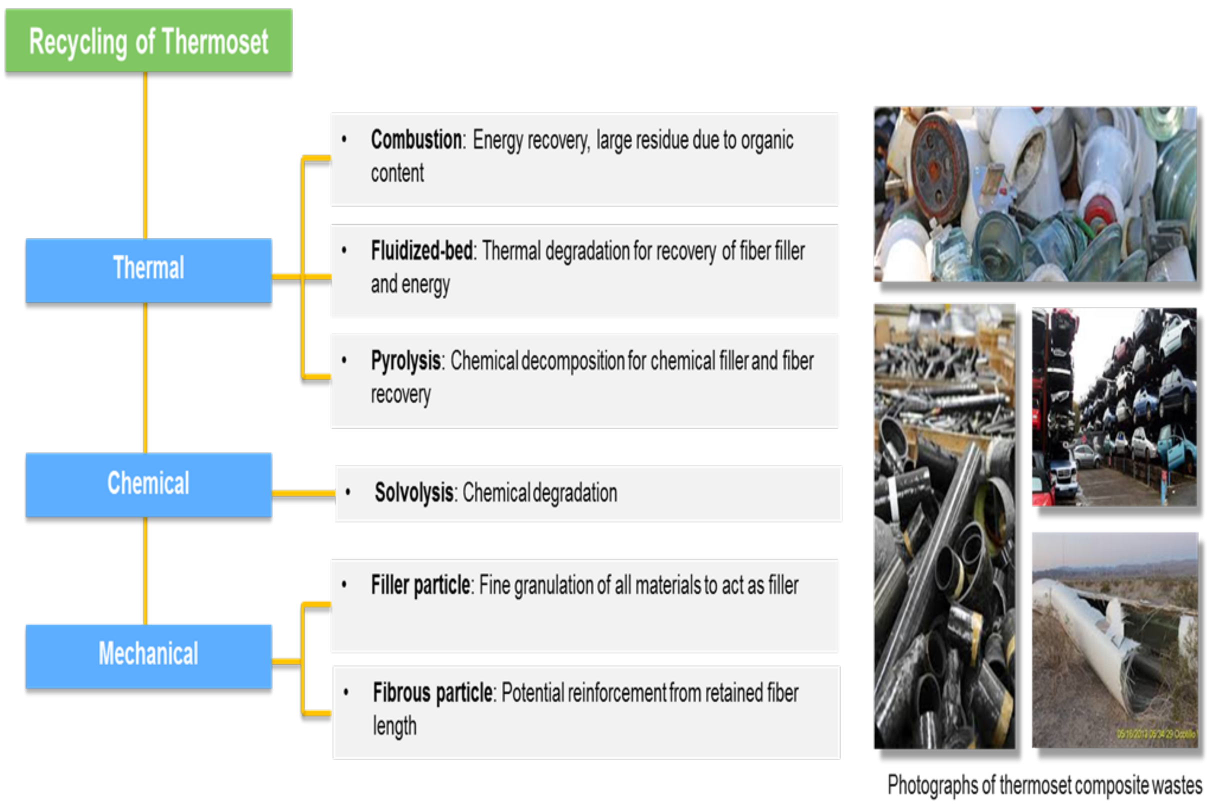

Figure 1: Typical Recycling Methods for Thermosets.

The Recyclamine® technology is a path breaking & patented innovation, which enables epoxy thermosets to become recyclable. Recyclamine® technology is expected to add tremendous value to PPP (people, plant & profit) and contribute to the circular economy by eliminating the greenhouse gas emissions during incineration of waste and lessen land filling & ocean dumping, by enabling recovery & recycling of thermoset waste into useful products.

1.2 The Concept:

Typically epoxy resins react with the curing agent or hardener to cross link and network into rigid infusible thermosets which then cannot be re-formed, re-used or re-cycled.

Recyclamine® technology is based on specifically engineered recyclamine® curing agents which enable cleavage points that converts thermosetting epoxies into thermoplastics under specific set of conditions. These cleavage points are reversible under specific condition and hence enable disintegration of the thermoset matrix. During this disintegration process all the valuable reinforcing components such as carbon fiber, glass fiber, kevlar®, plastic material in a thermoset composite, can be recovered and recycled. Concept is represented pictorially in Figure 2.

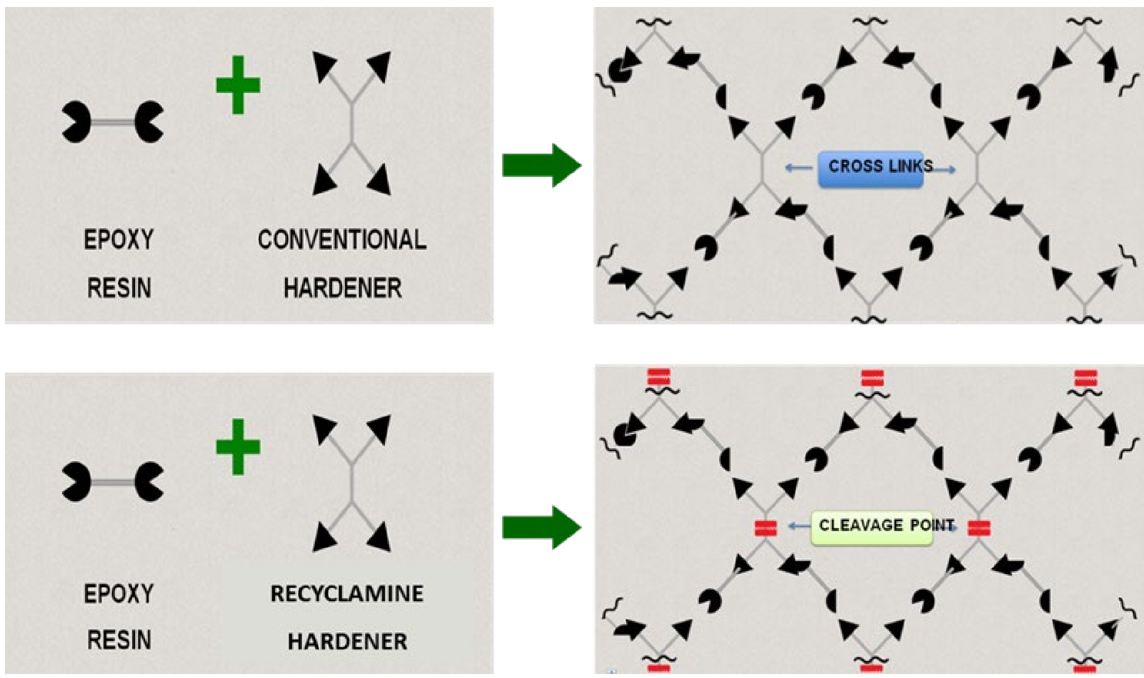

Figure 2: Schematic depicting Curing of Epoxy Resin Systems. (Conventional v/s Recyclable)

1.3. Recyclamine® Curing Agents:

The recyclamine® technology is a platform chemistry with series and wide spectrum of curing agents providing fast to slow reactivity & latency, low to high temperature resistance, chemical resistance and recyclability. The product portfolio comprises of over thirty five molecules classified into nine series based on the different chemical backbones and cleavable linkage (Figure 3) such as acetal linkage, a ketal linkage, a formal linkage, an orthoester, orthocarbonate linkage, or siloxy linkage.

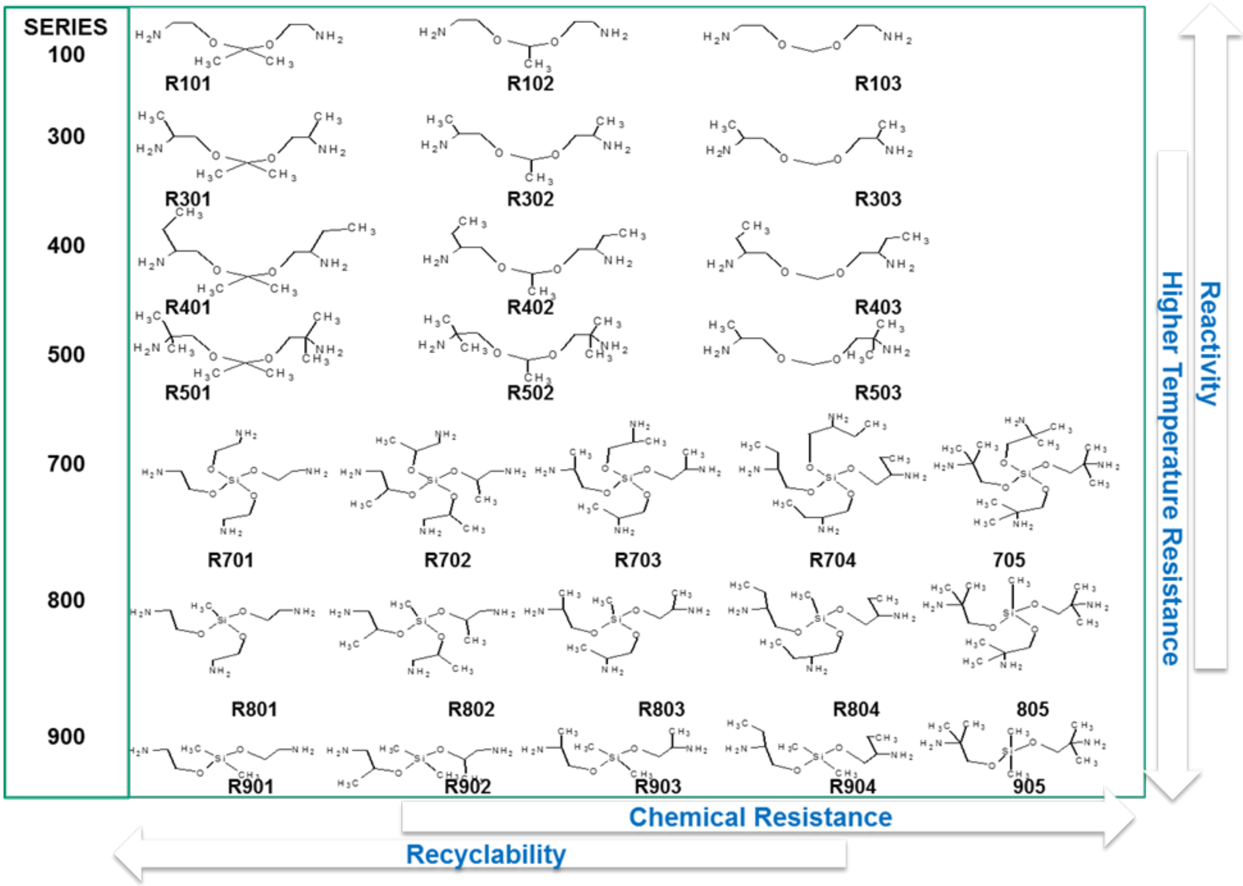

Figure 3: Recyclamine® Curing Agent Platform.

The physical and process properties of select Recyclamine® molecules (R10X,R30X, R50X and R80X) with Diglycidyl Ether of Bisphenol A (DGEBA) epoxy resin , epoxy equivalent weight 180-190 gm/eq. is shown in Table 1.

Table 1: Physical and Process Properties of Select Recyclamine®.

Property	Test Method	Unit	R101	R103	R301	R303	R501
AHEW (calculated)	-	gm/eq	40.5	33.5	47.5	40.5	54.5
Mixing ratio	-	by weight	100:22	100:18	100:25	100:22	100:29
Viscosity of hardener* @25°C	ASTM D 2196-05	mPa.s	8.83	4.92	8.10	7.29	10.7
Glass Transition Temperature (Tg) (80ºC/25 min. + 140ºC/ 4 hrs.)	ISO 11357-2	°C	97.79	92.83	115.66	95.78	105.62
Pot life (100 gms. mix @25°C)	ASTM D 2471	minutes	80.5	97.5	552	274	830

Property	Test Method	Unit	R 802	R 803	R 804	R 805
AHEW (calculated)	-	gm/eq	40.5	54.5	51.3	40.5
Mixing ratio	-	by weight	100:25	100:25	100:29	100:29
Viscosity of hardener* @25°C	ASTM D 2196-05	mPa.s	10.9	10.5	10.8	21.7
Glass Transition Temperature (Tg) (140ºC/ 4 hrs.)	ISO 11357-2	°C	99.36	105.99	97.56	128.39
Glass Transition Temperature (Tg) (80ºC/25 min. + 140ºC/ 4 hrs.)	ISO 11357-2	°C	105.62	106.02	106.32	132.17
Pot life (100 gms. mix @ 25ºC)	ASTM D 2471	minutes	114.5	416.5	616	723

* DGEBA Resin Epotec YD128 (EEW 180-190 gm./eq)

The Recyclamine® molecules exhibit low viscosity and wide range of reactivity, moderate glass transition temperature with DGEBA resin. These features were leveraged for development of recyclable laminating resin systems for polymer matrix composites replacing conventional polyamines such as aliphatic amines, polyether amines and cycloaliphatic. Selection of specific recyclamine® molecule was done based on the desired process and performance properties of the intended application.

2. EXPERIMENTATION

Epoxy resin systems comprising of epoxy resin and curing agent are preferred matrix materials in composite manufacturing processes such as wet-layup, resin infusion, vacuum assisted resin transfer molding (VARTM), prepregs, filament winding and pultrusion. Design and development of an epoxy resin system is largely dependent on the manufacturing process and the performance properties of the application. Process properties include initial mix viscosity of system, reactivity determined by the rise in viscosity with time and/or the working time determined by the pot life. Typically the epoxy resin component in an ambient cured system is a formulation comprising of liquid epoxy resins, diluents, modifiers and additives to impart the desired properties whereas the curing agent component is an polyamine or a blend of polyamines modified or un-modified.

Based on the process and performance properties of Recyclamine® with DGEBA resin (Table1), experiments were designed to develop recyclable epoxy resin systems for wetlay-up, resin transfer molding (RTM), resin infusion processes. For the resin formulation , commercially available Epotec® epoxy resins from Aditya Birla Chemicals ; DGEBA epoxy resin with epoxy equivalent weight 180-190 gm/eq (Epotec®YD127,YD128), Diglycidyl ether of Bisphenol F (DGEBF) with epoxy equivalent weight 170-180 gm/eq (Epotec® YDF170,YDF172) and epoxidized reactive diluents such as 1,4 butane di-ol diglycidyl ether (Epotec® RD103), 1-6 hexane di-ol diglycidyl ether (Epotec® RD107) and C12-C14 alkyl glycidyl ether (Epotec® RD108) were used. Defoamer and air release agent, BYK A-530 from BYK Chemie, was used in wet layup formulation to serve as a processing aid.

The curing agent formulation was developed by using select Recyclamine® (Figure 4) curing agents;2,2-bis (2-aminoethoxy) propane (Recyclamine® R101), 2,2-bis (2-aminopropoxy) propane (Recyclamine® R301), Tri (2-aminobutoxy) methyl silane (Recyclamine® R804) either standalone or by modifying to make reaction adduct with DGEBA resin.

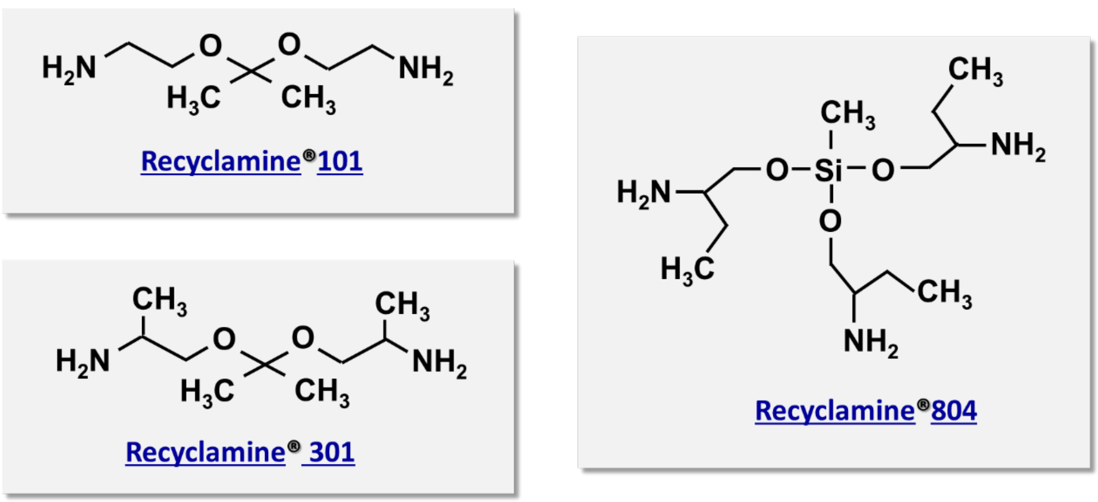

Figure 4: Recyclamine® Curing Agents Selected for Experimentation.

The resin systems were formulated considering the requirements of process and performance properties for specific applications such as sports & recreational composites, automotive composites and structural composites used for infrastructure-energy.

3. RESULTS

3.1 Characterization of Recyclable Resin Systems:

The physical, process and performance properties for typical batch of recyclable wet-layup system comprising of epoxy resin R1 and curing agent H1 are shown in table 2.

Table 2: Physical, Process and Performance Properties of Recyclable Wet layup System.

Properties	Test Method	Unit	R1 / H 1
Mixing ratio	-	by weight	100 :30
Viscosity @25ºC of resin	ASTM D 2196-05	-	1,520
Viscosity @25ºC of hardener	ASTM D 2196-05	-	44.7
Initial mix viscosity @ 25°C	ASTM D 2196-05	mPa.s	406.7
Pot life for 100 g. mix 25°C	ASTM D 2471	minutes	25.0
Glass Transition Temperature , Tg (50°C/ 2 hrs.)	ISO 11357-2	°C	53.44
Tack free time@25°C	-	hours	4

The wet lay-up system provided moderate processing viscosity of 406.7 mPas at 25^{0}C, pot life of 25 minutes and tack free time of four hours making it suitable for production of composites cured at ambient conditions.

The physical, process and performance properties for typical batch of recyclable RTM system comprising of epoxy resin R2 and curing agent H2 are shown in table 3. The system provided low processing viscosity of 237.9 mPas at 25^{0}C preferable for improved impregnation of reinforcement and developed glass transition temperature (Tg) of 81.61^{0}C when cured at 50^{0}C for 2 hours.

Table 3: Physical, Process and Performance Properties of Recyclable RTM System.

Properties	Test Method	Unit	R2 / H2
Mixing ratio	-	by weight	100 :26
Viscosity @25ºC of resin	ASTM D 2196-05	-	3,224
Viscosity @25ºC of hardener	ASTM D 2196-05	-	8.33
Initial mix viscosity @ 25°C	ASTM D 2196-05	mPa.s	237.9
Pot life for 100 g. mix @25ºC	ASTM D 2471	minutes	87.0
Glass Transition Temperature , Tg (50C/ 2 hrs.)	ISO 11357-2	°C	81.61

The physical, process and performance properties for typical batch of recyclable infusion system comprising of epoxy resin R3 and curing agent H3 are shown in Table 4. The system exhibited low initial mix viscosity of 190.0 mPas at 25^{0}C and slower reactivity; viscosity development with time and pot life of 561 minutes and 290 minutes respectively, which is advantageous for production of large to extra-large composite structures.

Table 4: Physical, Process and Performance Properties of Recyclable Infusion System.

Property	Unit	Test Method	R3/H3
Viscosity of resin @ 25°C	ASTM D 2196/ ISO 2555	mPa.s	1,114
Viscosity of hardener @ 25°C	ASTM D 2196/ ISO 2555	mPa.s	7.8
Mixing ratio	-	by weight	100 : 29
Initial mix viscosity @ 25°C	ASTM D 2196/ ISO 2555	mPa.s	190.0
Pot life for 1 kg mix @ 25°C (time to reach 60°C)	ASTM D2471	minutes	561
Viscosity development with time @30°C (up to 1,000 mPa.s)[(a)]	ISO 3219	minutes	290
Glass transition temperature, Tg (cured @70°C/ 6 hrs.)	ISO 11357-2	°C	78.79

3.2 Example of Manufacturing Composites from Recyclable Systems:

The recyclable epoxy resin systems were used for fabrication of composites using glass and carbon fabrics as the reinforcement. Resin infusion system, R3-H3, was used in making mold tool (Figure 5). 25 mm laminate comprising of 100 plies 100 gsm plain weave, 22 plies 160 gsm plain weave and 16 plies 1200 gsm stitched tri-ax glass fabrics was infused at 40˚C, cured at 60˚C and then post cured 8 hours at 80˚C to attain optimum glass transition temperature (Tg) and performance properties.

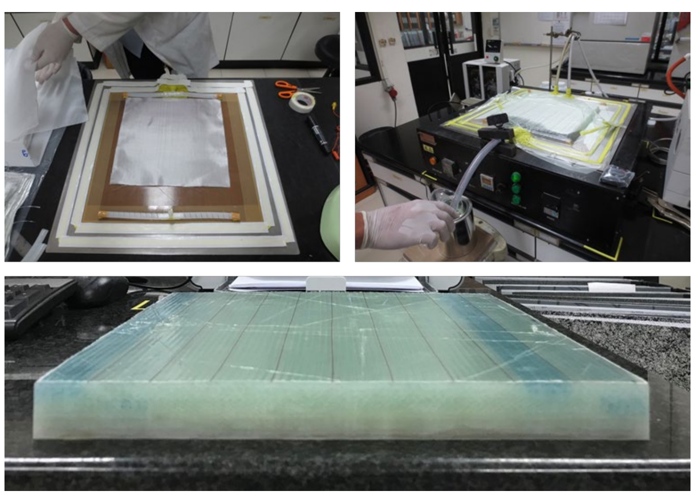

Figure 5: Production of Glass Fiber Laminate using Recyclable Infusion System.

The recyclable RTM system was used for the production of surfboard fins (Figure 6).Woven glass fabric plies and core material were cut to size and layed-up in release coated epoxy mold tool. RTM injection of fin with pigmented recyclable epoxy RTM was done at ambient conditions at Cobra International Company in Thailand.

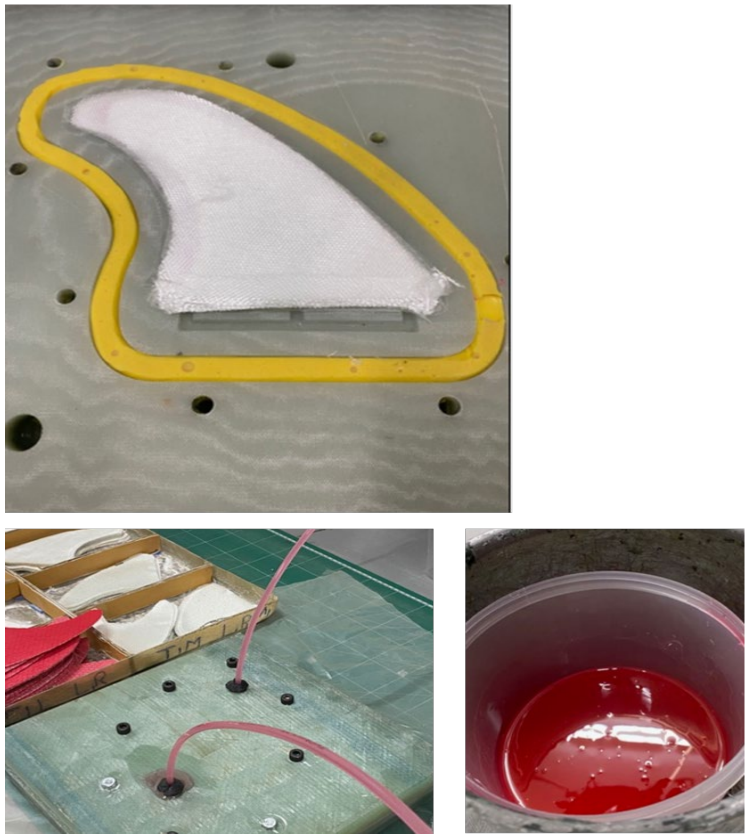

Figure 6: Production of Composite Fin using Recyclable RTM System.

3.3 Recycling & Recovery of Composite:

The mold tool and composite fins made from recyclable systems and glass fiber reinforcement were rinsed in an acetic acid solution at 80°C temperature for 2 hours. Within 1 hour the specimen started to soften due to cleavage of epoxy resin matrix in the acetic acid solution and in 2 hours, the epoxy resin matrix from the mold tool and composite fins completely cleaved and dissolved in the acidic solution (Figure 7).The solution containing dissolved resin matrix was filtered and separated away from the reinforcement material.

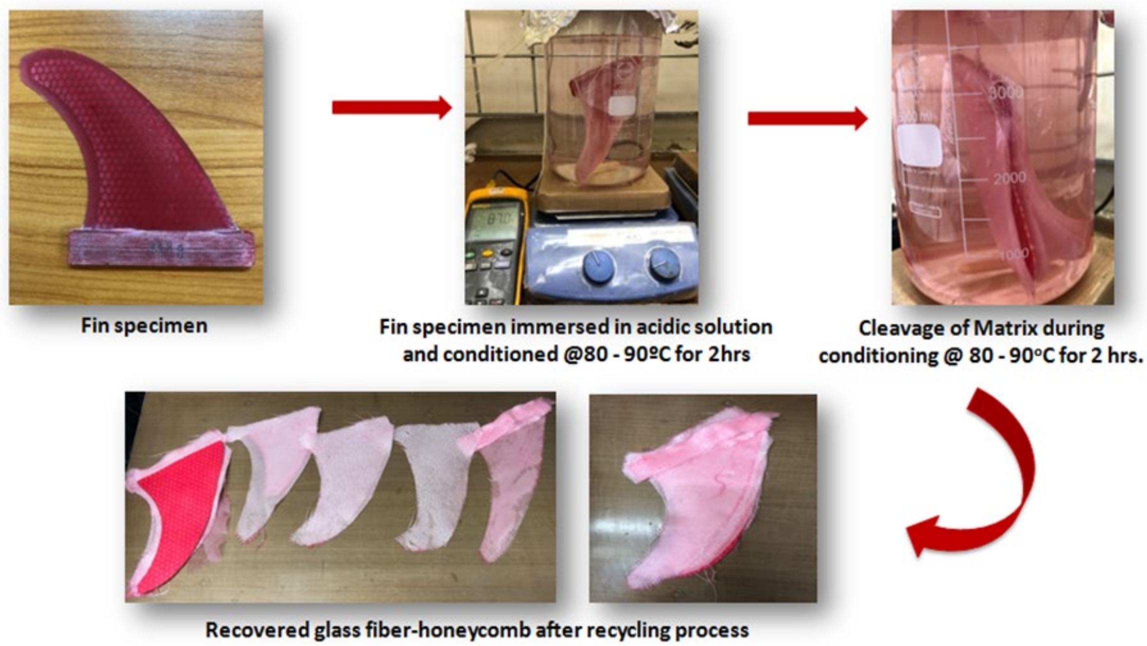

Figure 7: Recycling Process of Composite Fin.

The reinforcement material was subsequently dried and recovered for reuse, while the epoxy matrix dissolved in acetic acid solution was neutralized and coagulated to form thermoplastic polymer (Figure 8).

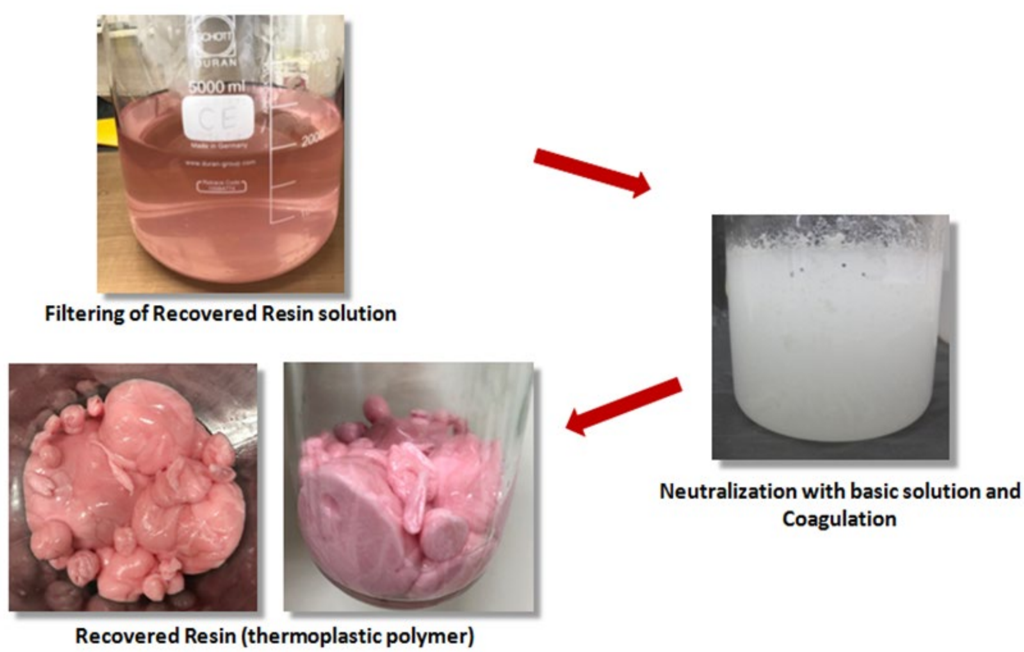

Figure 8: Recovery of Thermoplastic Polymer.

The recovered thermoplastic polymer was characterized Tg by differential scanning calorimeter and degradation temperature by thermo gravimetric analyzer (TGA).

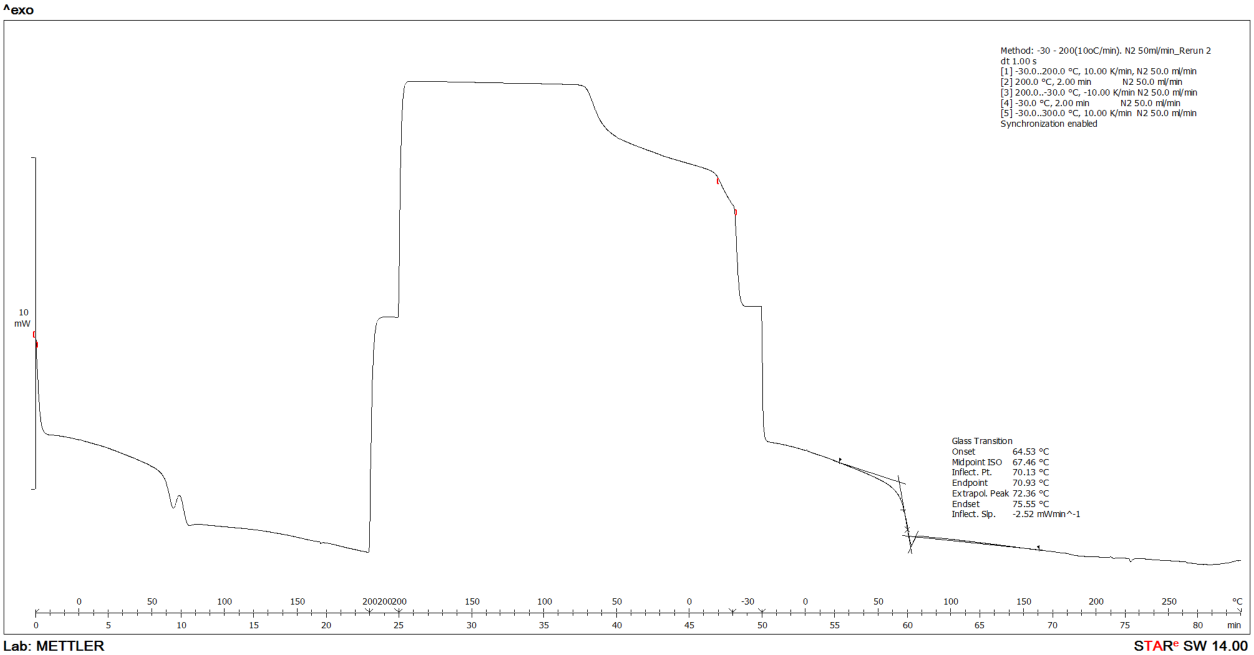

Figure 9: Profile of Glass Transition Temperature of Recovered Thermoplastic.

The Tg was measured as 67.46 ^{0}C (Figure 9) and degradation temperature was measured as 373.77ºC (Figure 10).

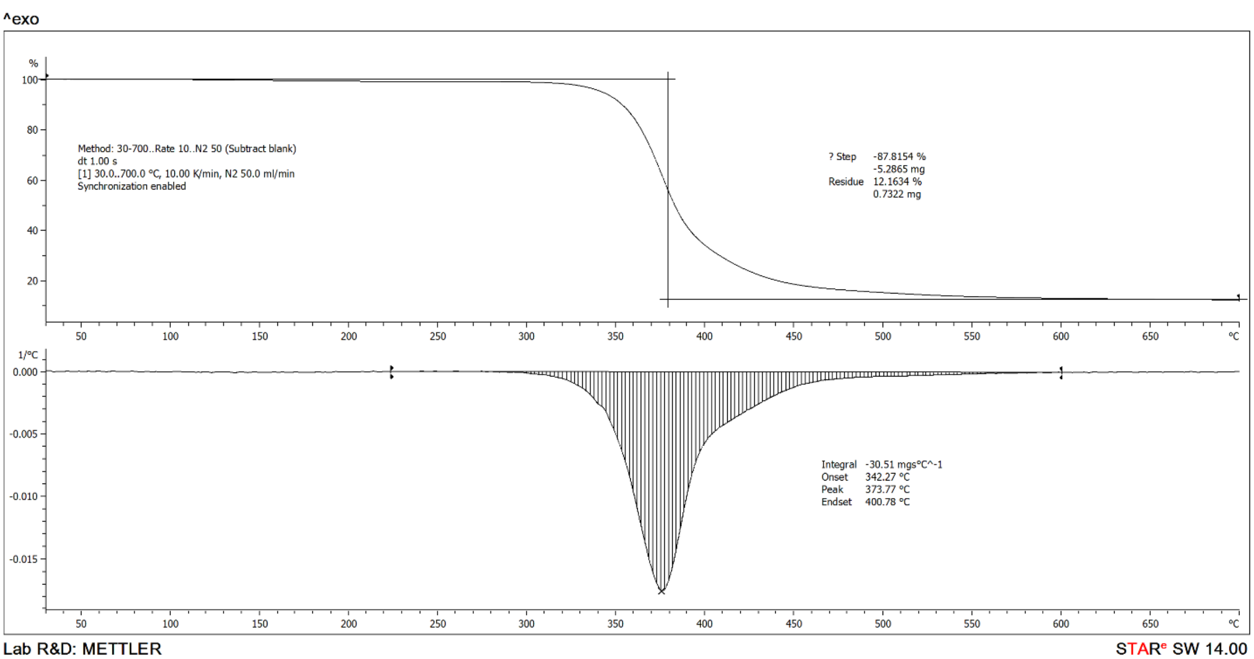

Figure 10: Profile of Degradation Temperature of Recovered Thermoplastic.

Recycling of the recovered thermoplastic was done by compounding with polyethylene in weight ratio 80:20 and injection molded to prepare foot strap insert used in surfboards (Figure 11).

Figure 11: Footstrap Insert from Recovered Thermoplastic Polymer.

4. SUMMARY & CONCLUSIONS

Recyclamine® curing agents were used in development of ambient cured recyclable epoxy resin systems for wet layup, RTM and infusion processes. The systems were characterized by studying the physical, process and performance properties and further used in manufacturing composite; mold tool laminate by infusion process and fins by RTM process, as an example. The composite parts manufactured were recycled to recover, glass fabric reinforcement and matrix as thermoplastic resin. The thermoplastic resin was compounded with polyethylene to produce a representative part, while the reinforcement recovered from recycling was dried for reuse.

The recycling and recovery of glass fiber epoxy thermoset composite was successfully demonstrated which validates the sustainable-closed loop concept of Recyclamine® chemistry. The results also confirm that the concept can be extended to all types of polymer composites, reinforced with synthetic fibers or natural fibers.

Additionally , the process and performance properties of recyclable resin systems indicate the potential of Recyclamine® curing agents to replace conventional polyamines such as aliphatic amines, polyether amines and cycloaliphatic used in typical composite formulations as well as the suitability to use recyclable epoxy systems for applications in sports & recreational composites, automotive composites and structural composites used in infrastructure-energy.

The key environmental impact created by Recyclamine® based epoxy systems not only relates to the end of life recycling and reuse but also to the reduction in carbon foot print , thus in the era of circular economy, the Recyclamine® curing agents offer novel path-breaking solutions for a sustainable world.

5. REFERENCES

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