SUMMARY & CONCLUSION

Saturated and unsaturated polyester and their montmorillonite filled nanocomposites derived from glycolyzed PET are developed by using various polymerization techniques.

1. Synthesis of Unsaturated Polyester from Glycolyzed PET.
2. Synthesis of Unsaturated Polyester nanocomposite (Simultaneous mixing).
5. Synthesis of Saturated Polyester from Glycolyzed PET.

Waste PET is glycolyzed along with virgin PET. A higher proportion of virgin PET in the mixture has the ability to consume more glycols during glycolysis. This gives rise to a glycolyzed PET (GPET1), which contains a lesser amount of free glycol and shows the highest hydroxyl value. During polyesterification of the polyester diol (GPET) with maleic acid, the degree of polymerization (DPn), and extent of reaction is observed to be increasing while acid value decreasing with an increase in the virgin PET content in the mixture. This is believed to be due to the increasing presence of BHET in the GPET.

Response surface methodology (RSM) was used for predicting the optimal condition of glycolysis time and temperature in the glycolysis of PET scrap. Central composite rotatable design (CCRD) for two variables at four levels was chosen as the experimental design. The data obtained from measurement of properties was fitted as a two variable second order equation and were plotted as 3D surface plots using programme developed in MATLAB v.5. Analysis of variance (ANOVA) was used to evaluate the validity of model.
The optimum operating conditions for glycolysis time and temperature were 6.50 h and 180 °C. Under these optimal conditions, the hydroxyl value and glycolysis conversion percentage was 37.60 mgKOH/g and 95.67 % respectively at the 0.97 desirability level. Whereas the acid value and average molecular weight at the same desirability level was 15.4 mgKOH/g and 695 g/mol respectively.

The solvent resistance properties of the unsaturated polyester and their montmorillonite filled nanocomposites are studied in acetic acid through equilibrium swelling method at different temperatures. The kinetics of sorption is studied by using the equation of transport phenomena. The values of ‘n’ in solvent transport equation are found to be below ‘0.5’, showing the non-Fickian or pseudo-Fickian transport in the polymer. The dependence of diffusion coefficient on composition and temperature has been studied for all polymeric samples. The diffusion coefficient in unsaturated polyester samples decreases with an increase in unsaturated acid content. There is sudden rise is observed in diffusion coefficient for the 100UP0 sample. The nanocomposite samples show low diffusion coefficient than corresponding pristine polymer and it decreases with an increasing in nanofiller up to 4 wt %. The diffusion coefficient, sorption coefficient and permeation coefficient increase with an increase in temperature for all the samples. The crosslink density for neat polymer with varied unsaturated acid content ranges from 2.98 to 3.52 ×10^5 mol/cm³. For the nanocomposite samples it ranges from 3.70 to 5.72 × 10^5 mol/cm³.

Kinetics of swelling and sorption behavior of unsaturated polyester nanocomposite (based on glycolyzed PET, maleic anhydride, styrene, and montmorillonite) synthesized by two different mixing methods, simultaneous and sequential is studied in acetic acid at different temperatures. The values of n in the transport equation are found to be below 0.5,
showing non-Fickian or pseudo-Fickian transport in the polymers. The dependence of diffusion coefficient on the mixing methods and temperature has also been studied for the unsaturated polyester nanocomposite. The diffusion coefficients in simultaneous mixing samples decrease with an increase in the mixing time in the samples. In case of the sequential mixing samples, the diffusion coefficient increases with an increase in mixing time. The diffusion coefficient increases with an increase in temperature for all the unsaturated polyester nanocomposite samples. The sorption coefficient increases with an increase in the mixing time for all the samples synthesized by in-situ mixing method. The crosslink density (calculated from the CH₃COOH swelling) ranges from 5.014 to 7.092 × 10² mol/cm³ for simultaneous mixed samples and 5.212 to 7.192 × 10² mol/cm³ for sequentially mixed samples.

The post consumer polyethylene terephthalate (PET) waste bottles were glycolyzed for precursor of unsaturated polyester resin and their montmorillonite filled nanocomposites. The glycolysis product (hydroxyl terminated oligomers) was converted into unsaturated polyester resin with varied acid content. These resins were miscible with styrene and could be cured using peroxide initiators to produce thermosetting unsaturated polyester. Nanocomposites composed of unsaturated polyester matrix and organically modified clay was prepared by in-situ polymerization. These were characterized for thermal and dynamic mechanical properties. Transmission electron microscopy (TEM) was also used to study the morphology at different length scales and showed the nanocomposites to be compromised of a random dispersion of intercalated/exfoliated aggregates throughout the matrix. With an increase in unsaturated acid content (for fixed content of clay), the value of storage modulus (E’) varies from 2737 MPa to 4423 MPa. The glass transition temperature of these
nanocomposites ranges from 54 to 78 °C and the crosslink density ranges from $3.70 \times 10^5$ to $5.72 \times 10^5$ mol/m$^3$. The XRD of modified montmorillonite exhibits a peak, which vanishes completely in the polymer nanocomposites. Thus, the XRD results apparently indicate a distortion of the platy layers of nanofiller in the unsaturated polyester nanocomposites. The nanocomposites show higher (2737 to 4423 MPa) compared to the pristine polymer (2693 MPa). From thermogravimetric analysis (TGA), all the nanocomposites are stable up to 200 °C and show two-stage degradation.

A new system of saturated polyester and their nanocomposite synthesized from glycolyzed PET with varied composition is investigated for the sorption and diffusion studies in water. The kinetics of sorption is studied by using the equation of transport phenomena. The values of ‘n’ in solvent transport equation are found to be below ‘0.5’, showing the non-Fickian or pseudo-Fickian transport in the polymer. The dependence of diffusion coefficient on composition and temperature has been studied for all polymeric samples. The diffusion coefficient in saturated polyester samples decreases with an increase in glycolyzed PET. The nano-composite samples show less diffusion coefficient than pristine polymer and it decreases with an increasing in nano-filler upto 4% by weight. The diffusion coefficient increases with an increase in temperature for all polymer samples. The sorption coefficient shows a little change with variation in composition as well as temperature for all the samples and it is in a range of 1. The activation energy for diffusion and permeation is positive for all the samples. The heat of sorption is also positive for all the samples, indicating Henry type mode of sorption.

Saturated polyester resin, derived from the glycolysis of PET is examined as an effective way for PET recycling. The GPET was reacted with the mixture of phthalic
anhydride and ethylene glycol (EG) with varied composition and their reaction kinetic were studied. During polyesterification of GPET with varied composition, the degree of polymerization (DP$_n$) and extent of reaction (p) is observed to be increased, while acid value decreased with an increase in the GPET content in the mixture. The well defined order maintained up to 50 % GPET content beyond it, the (DP$_n$) and extent of reaction decreased with time. The characterizations like water vapor transmission rate (WVTR), wide angle X-ray diffraction (WAXRD), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) of nanocomposites have also been investigated. To examine exactly the dispersion of the clay layers in the saturated polyester matrix, transmission electron spectroscopy (TEM) studies were carried out. Some of clay particles were well dispersed in the polyester matrix and some of them were agglomerated. It is noticeable that addition of GPET resulted into further increased in T$_g$. The T$_m$ for all nanocomposites with 50 % GPET content was 10-15 °C higher as compared to the standard PET (STDPET) sample. When the organoclay in polyester matrix reached 4 wt % the storage modulus had increased about 2.0 fold over that of STDPET. It is notified that the T$_g$, measured by loss modulus peak for all nanocomposite samples was 10-15 °C smaller than T$_g$ measured by DSC.

In conclusion, it is observed that the polyester from recycle PET waste synthesized by in-situ polymerization are suitable due to their superior properties. Their dynamic mechanical and thermal properties are up to the mark. The unsaturated polyester (GPET waste) have the best visco-elastic properties, which make them suitable for the shape memory and damping applications. The nanocomposites from GPET waste have shown remarkable increase in the modulus and transition temperature with respect to other neat polymers. They show higher thermal stability and two stage degradation. The incorporation
of the 4% nano-filler gives the best properties. The GPET based polyester and their nanocomposites are very good alternative for the various applications in lieu of petroleum based polymers. Various complex structures, such as tubes, panels, and automotive parts that are currently made from petroleum-based plastics might be replaced by these thermoset plastics. The swelling technique is a commonly used method to determine various coefficients such as diffusion, sorption, and permeability coefficient. These coefficients give an idea about the use of polymers in various applications, such as membranes, ion-exchangers, controlled release systems, packaging, microchip manufacturing, etc. The study of water sorption in polymers is important for many applications. Water is probably the single most important factor in governing microbial spoilage in foods. Barrier polymers are widely used in food, beverage, and other packaging industries. Some of the their advantages over traditional packaging materials like glass, paper, and metals are flexibility, light weight, toughness, versatility, and printability. These nanocomposites possess much higher mechanical properties and thus may find applications where engineering plastics are currently being widely used.

Unsaturated polyester resins (UPRs) are one of the most important thermoset materials used in composites industry for the preparation of molding compounds, laminates, coatings, and adhesives. UPRs have made significant structural and performance advances which resulted in their broader application in automotive, building, construction, and marine industries. One of the key advantages of UPRs is the ease of fabrication, which results in low production costs. This is mainly attributed to easily controllable and fast cure processes, which proceed via free radical polymerization mechanism.
Based on the dynamic mechanical, thermal, morphological and sorption properties of nanocomposite prepared by using recycled PET-bottles indicates its possible use in food packaging. However, further research related to the use of these nanocomposites in packaging of fresh fruits, vegetables and flexible packaging of thermally processed food products are required.