

# Development and Assessment of Polymeric Laminate blended composites Reinforced with Bi-Woven Aramidic Fiber

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## ABSTRACT

In the present paper evaluates laminated aramidic bi-woven fibers reinforced in polyester-vinylester blended composites. The Duo polymers, polyester-vinylester were blended using in situ polymerization technique. Four planar layers were made simultaneously and keeping one over another and each layer make sure to be weighed off 15% were maintained in all layers with different orientations. Pre-assumed Layer-1(50/50) 50 %, 0°; Layer-2(35/35/30) 35 % 0°, 35 % +45°, 30 %,0; Layer-3 (25/50/25) 25 % 0°, 50% +45°, 25-45°; Layer-4 (25/25/25/25) (2 5% 0°, 25 % +45°, 25 % -45°, 25 % 90°). Tthe composite was prepared with the help of hand layup technique. Test ready specimens were the help of shearing machine in accordance with ASTM. It was observed that, polyester and vinylester had good miscibility makes combined solid material. Flexural strength, tensile strength was improved up to 3ed layer, decreases after, whereas flexural modulus and tensile modulus were linearly increased up to 4<sup>th</sup> layer. Thermal stability and glass transition temperature were also found satisfactory for all the laminated layers. Chemical resistance was good for the entire chemical except toluene.

**Keywords:** laminates; polymer blends; thermomechanical; chemical resistance

## 1. INTRODUCTION

In the field of reinforcements the new developments in long fiber for high performance are aramidic, carbon or polyethylene fibers. The mixing together of different polymers has been carried out for many years for various purposes. Rubbers have been used to flexibilise rigid plastics. Rigid plastics have been used to stiffen rubbers. Many adhesives, sealants, and coatings have been based on blends of polymers [1-5]. We have been dealing at all times with heterogeneous rather than the homogeneous systems. It even appears that many of the successful results of mixing polymers are attributed to the properties obtained from two phase systems. The earliest blends were prepared by exploiting the natural miscibility of the components. Good examples of blends of polyvinylchloride and acrylonitrile rubber or polyphenylene-ether (PPE) with high impact polystyrene (HIPS) the miscibility was the main

criterion for blending. For example the disadvantages of PPE (processability and impact stress) are compensated for the advantageous properties of either polyamides or HIPS. In recent years blends are increasingly used as a base for either foams or composites. Better component interfacial properties either via sophisticated chemistry or reactive processing made this step possible. Reinforced grades of polymer blends are also used in commercial purpose. Polymer blends and composites will certainly be continuous as lively research areas greater understanding will allow controlled manipulation and optimization of properties. Vinyl ester is a copolymer thermoset resin produced by the esterification of an epoxy resin with unsaturated monocarboxylic acid.

The reaction product is then dissolved in a reactive solvent, such as styrene, to 35-45 % content by weight. Vinyl ester can be used as an alternative to unsaturated polyester and epoxy materials in matrix or composite material because its distinctive characteristics, strength and bulk cost lie intermediately between polyester and epoxy [5-15]. Vinyl ester has low resin viscosity, less than polyester and epoxy, but the epoxy-based vinyl ester has remarkable corrosion resistance, physical properties and improved adhesion compared to polyester due to their chemical composition and the presence of polar hydroxyl and ether groups. Simulated vinyl ester chains are 65 % epoxy and 35 % styrene; Vinyl ester resin systems have other challenge: poor resistance to crack propagation, brittleness and large shrinkage that occurs during polymerization. Unsaturated polyester offers excellent mechanical, thermal and corrosion resistant properties and is also low. Mixing polyester and vinyl ester resins would certainly bring out solid material which has combine properties and that too when it is reinforced with aramidic (also called aramid) fibers will leads to unique properties. Because, aramid fibre reinforced polymer with thermoset polyester resin is an attractive material that is economically desired. Its application at low temperatures and under service terms is easy, when this material is compared to advanced polymer composites with complex molecule structure, high strength and working under terms of difficult service. This material is preferred due to the superiority of polymer mixed material, because it is easy to produce and at low cost, more than advanced engineering applications. It is being questioned the developed and improved properties of this material in present. Epoxy/ polyester polymer blended nanocomposites and its effect of nanoparticles on thermal and mechanical properties were studied already. It was noted that the critical stress intensity factor increased with particle size. Thus, the poor resistance to crack propagation of epoxy resin can be improved by the addition of rigid filler particles as a second phase.

Work on particle filled fibre composite indicates that the toughening of virgin materials is only marginally improved. The use of hybrid fibre reinforced polymer matrix (HFRP) nanocomposites in engineering applications has developed significantly developed in recent years. The applications of these materials include space and the reinforcement of automobile applications. The main aim in using the composites is, generally, to modify the properties in order to extend the life span of usage. The use of nanocomposites as replacements for conventional materials such as steel and timber is based on considerations including weight savings, tailored performance characteristics, and potential increases in overall durability and longevity. Carbon/vinylester and carbon/epoxy systems were often chosen due to easy processing and potential durability considerations. Yet, much remains to be described in terms of fundamental understanding of ageing and degradation mechanisms in the fields of the repair, strengthening and retrofit of concrete structures. The main short-term damage mechanisms of HFRP composites are known better, while there are many gaps regarding the long-term projections for these mechanisms [16-29]. The effects of coupling constraints are seldom taken into account especially in the field of engineering applications.

In order to address the various issue of the above, authors focused on the aramidic fiber reinforced polymer-polymer blended composites. Composites were prepared in such a way that woven type aramidic fibers cut in accordance with cast mould size of four different layers were cumulated simultaneously. Laminated/blended composites were characterized on mechanical, thermal and chemical resistance properties.

## 2. MATERIALS & METHODS

Polyester (Ecmalon 9911, Ecmas Hyderabad, with 2 % cobalt accelerator, catalyst 50% methyl ethyl ketone peroxide (MEKP) in 10 % DMA solution, ratio of the resin/accelerator/catalyst: 100/2/2. The resin has a density of 1335 kg/m<sup>3</sup>, Young's modulus of 450 MPa, tensile strength of 15.3 MPa and elongation at break of 3.3 %. The vinylester resin used was HPR 8711 grade, a Bakelite Hylam product. Methy ethyl ketone peroxide (MEKP), Co-napthenate and N,N-dimethylamiline were used as the catalyst, accelerator and promoter respectively. The thermal characteristics TGA, DSC measured on blended polymer nanocomposites using SDT Q600 TGA/DSC (TA Instruments) at a rate of 10 °C/min under nitrogen flow measurements were carried out at 20 °C temperature, 40 % relative humidity. A JEOL JSM-6400 JAPAN scanning electron microscope at 15 kV accelerating voltage was equipped with energy dispersive spectroscopy (EDS) to ascertain the fiber/filler interfaces with the main modified matrix. Fractured specimen surfaces were gold-coated and the fractures surface was observed using a scanning electron microscope. The fractured surfaces were gold-coated with a thin film to increase the conductance. The FTIR spectra of the powders of the samples were run on an ABB-Bomem FLATA-2000 model spectrophotometer using KBr pellets. The concentration of the fabric powder was maintained at 1 % in KBr. Flexural properties were measured in accordance with the procedures in ASTM D790. Flexural strength is a measure of how well, a material resist bending. Values for flexural strength and flexural modulus are reported in MPa. Impact properties were measured in accordance with ASTM D256. For chemical resistance test samples were cut like standard sizes (i.e. 10 X 10 X 3 mm<sup>3</sup>) on par with ASTM G 543-87. The effect of some acids, alkalis, and solvents, that is, glacial acetic acid, nitric acid, hydrochloric acid, ammonium hydroxide, aqueous sodium carbonate, aqueous sodium hydroxide, carbon tetrachloride, benzene, distilled water, and toluene were used on the matrix and the hybrid composites were studied. In each case, the samples were pre-weighed in a precision electrical balance and dipped in the respective chemical reagents for 24 h. Then they were removed immediately, washed in distilled water, and dried by pressing on both sides with a filter paper at room temperature.

### 2. 1. Laminated Composites preparation

Composites were prepared using hand layup technique. A mold was prepared on par with ASTM dimensions, and it was coated with a mold releasing agent (poly-vinyl-alcohol) for easy removal of casting. Predetermined dimensions of 300 X 300 mm<sup>2</sup> aramidic woven fiber were cut with appropriate scissors and make sure to ensure flat surfaces of mats. Mats were mercerized for about 2h under tensile loading to obtain the flat surfaces. Polyester and vinylester by parts of 80 wt. % and 20 wt. % by weight respectively were mixed together with spatula for about 30 min under the presence of temperature just above the atmospheric. Then the accelerator/catalyst/promoter (100:2/2/2) parts by weight was added to the modified polyester/vinylester mixture. Mat should be place in the mould cavity before blended solution

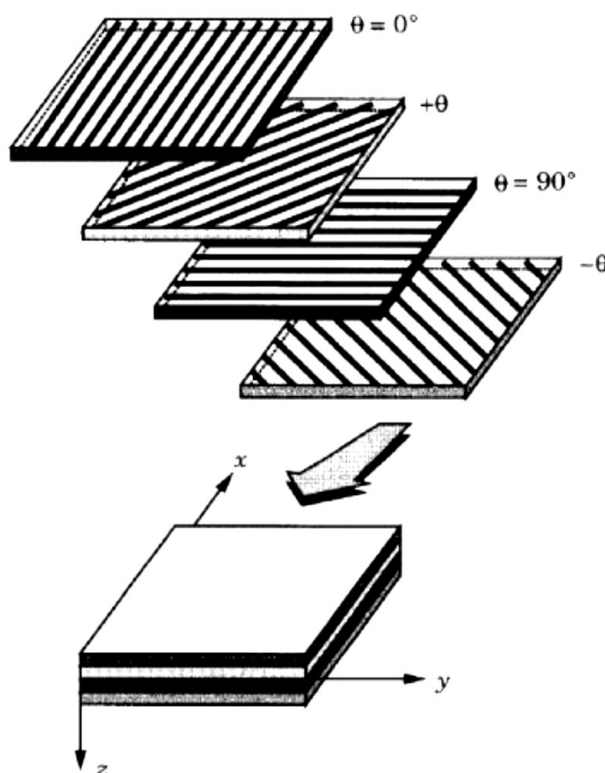
to be poured on par with the orientations mentioned in the above for different layers. Blended mixture was poured into the mould cavity in such a way that mat should completely drowned with blended solution and yet it has to be in the approximately at the centre place if it is asked to be single layer-1. Air was removed with the help of vacuum machine. Brush and roller were used to impregnate fiber. The closed mold was kept under pressure for 24 h at room temperature. To ensure complete curing, the composite samples were post-cured at 80 °C for 45 min. Now the single layered laminated polymer blended composites is ready. In order get to two layered laminated composite make sure to keep two mats in the mould cavity one upon the in the orientations mentioned above and then same blended solution has to be poured in to the mould. Similarly three and four layered laminated composites were prepared. Specimens of required size were cut out from the post cured laminated composites for further characterizations as per ASTM standards.

### 3. RESULTS AND DISCUSSIONS

Four different laminated layers were coded as mentioned below. Layer-0 ( 0/0)no fiber was inserted); Layer-1 (50/50) 50 %, 0°; Layer-2 (35/35/30) 35 % 0°, 35% +45°, 30 %,0; Layer-3 (25/50/25) 25 % 0°, 50 % +45°, 25-45°; Layer-4 (25/25/25/25) (25% 0°, 25 % +45°, 25 % -45°, 25 % 90°; ( example:(25/25/25/25) first ply is 0° and the second ply is +45°; third ply is -45°: fourth ply is 90°. Aramid fibers were dispersed into the polymer blend in the form of four layers as mentioned above as shown in the Fig. 1.

Improvement of flexural strength as a of laminated layers is shown in Table 1. Flexural strength for layer-0 (means there is no ply in the blend) laminate was 46 MPa approximately. Flexural strength was significantly increased from layer-1 to layer-3 linearly, on other hand after 3ed layer laminate strength becomes reduce. In the layer-4 flexural strength was 60 MPa. Reason for reduced strength is when no of layers are increased consequently resin might have not wetted in all the places, due to this reason, in the same places there will be a entrapment of air make the crack initiation had occurred due to poor stress transfer.

The increase in strength was due to good fiber matrix interactions, which was largely due to the orientation of fiber plane structures might have enhanced ability of the fiber resistance. Planar type fibers have higher aspect ratio and this increases the wet ability of the fibers by the matrix, thus creating fewer micro voids between the fiber and matrix. Another reason is if layers are not perfectly bonded together as a result of this cohesion becomes poor between the matrixes and layers. Another reason is when stress is being transfers from fiber to matrix, in the process as matrix does not resist large stress, automatically crack will initiate. Another reasons are the material of each layer is linearly elastic and has three planes of material symmetry (i.e., orthotropic) (restriction),each layer is of uniform thickness (restriction), the strains and displacements are small (restriction), the transverse shear stresses on the top and bottom surfaces of the laminate are zero (restriction). Up to some extent matrix could have accommodated the resin, so much so that strength was increased up to layer-3. When fiber layers were dispersed in to the matrix with different orientations the toughening effect of the composites will raise from the occasion. This could enhance the flexural modulus of the blended composite. Tensile strength was increased significantly from 0-3 laminates, whereas reduces suddenly at layer-4.



**Figure 1.** A laminate made up of lamina with different fiber orientations.

**Table 1.** Variation of flexural strength and modulus and tensile strength and modulus of different layers of laminated blended composites.

No of laminated layers	Flexural strength (MPa)	Flexural modulus (GPa)	Tensile strength (MPa)	Tensile modulus (GPa)
Layer-0	46±1.34	1.6±1.02	25±1.53	1.3±2.47
Layer-1	53±2.12	2.4±2.10	32±2.01	1.4±2.36
Layer-2	64±1.45	2.6±2.46	36±2.14	1.6±2.48
Layer-3	65±2.91	2.7±2.16	39±2.67	1.7±2.74
Layer-4	60±2.67	2.8±2.74	35±2.00	1.9±2.79

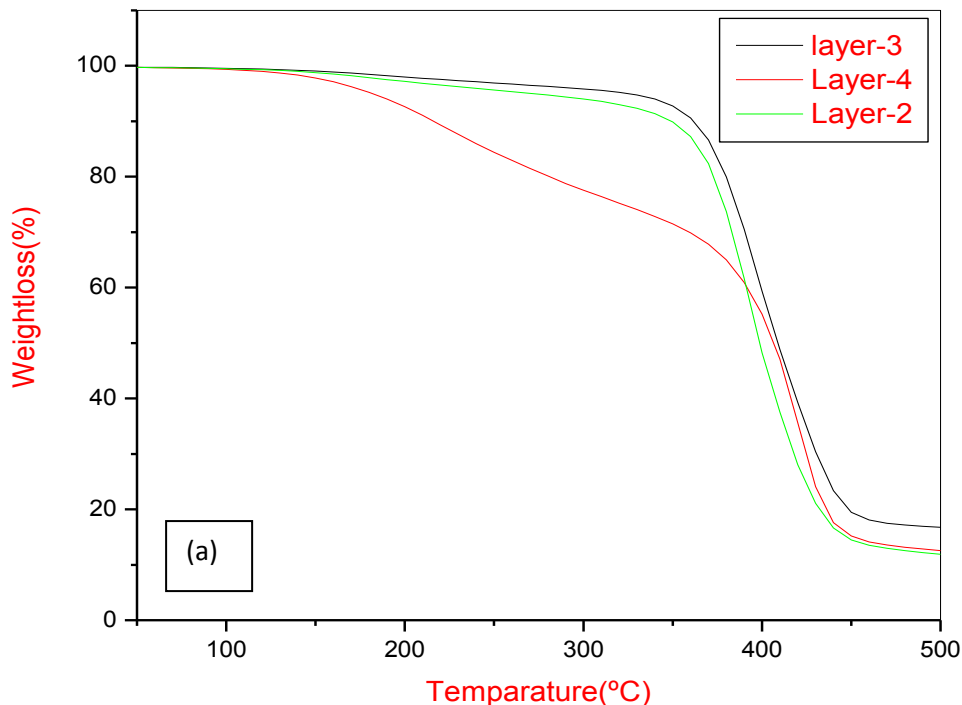
The decrease in tensile strength at layer-4 laminate could be attributed to poor adhesion between the layers and the modified matrix, which promotes the microcracks formation at the interface. A larger layer content results in more and probably larger in more void formation during processing, which leads to micro-crack formation under loading and therefore reduces the tensile strength. Park and Jang [15] study highlighted that stacking pattern of the different components in hybrid laminated composite play an important role in influencing the mechanical properties of the hybrid composites. Idicula et al. [5,6], Khalil et al. [7] and Mohan et al. [12] reported that layering pattern of the fibers in hybrid composite effect tensile strength and modulus of the hybrid composites. Various researcher studied

synthetic fibre/natural fibre based hybrid composite but natural fibre based hybrid composites are recent phenomena due to environmental concern.

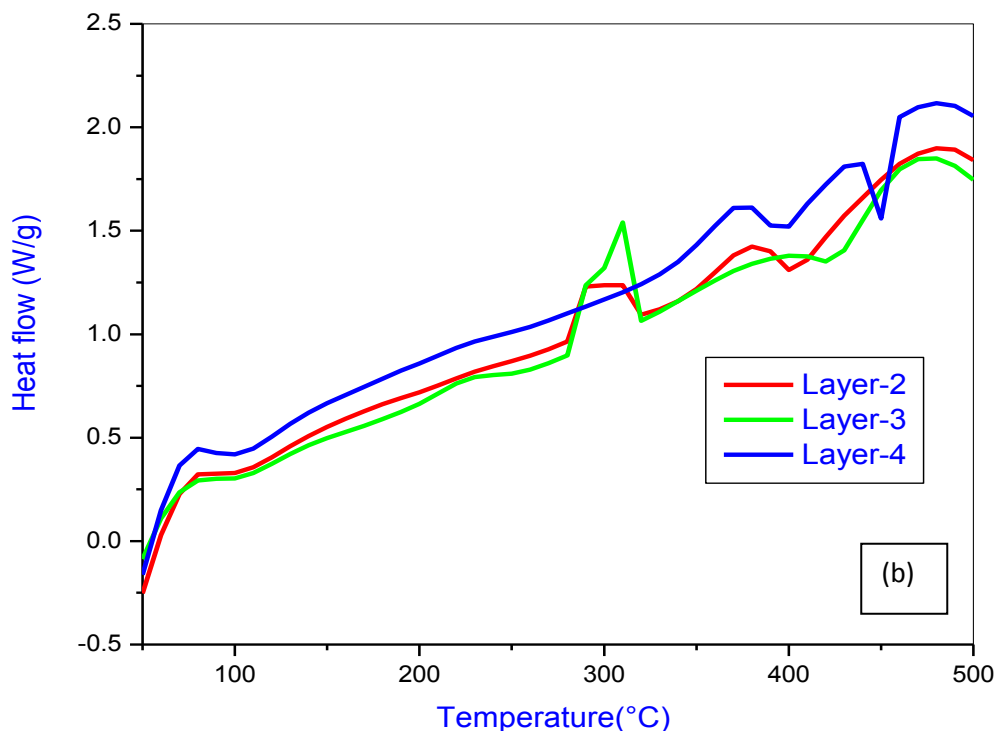
Moving on to, the variation of tensile modulus of blended laminate composites are tabulated in the Table 1, in which tensile modulus significantly increased from 0-3 layers, but decreased at layer-4. The attributed reasons are, when inclusion of filler in the matrix leads to significant increase in tensile modulus. The addition of rigid layers increases the stiffness in the matrix. This development is well explained by the percolation theory. According to this theory there is a matrix zone around each filament affected by stress concentration. If the distances between filaments are small enough, the zones join together and form a percolation network, which increase the tensile modulus [11,13,19-29].

Thermal stability of various laminated layers as a function of temperature as shown in Fig. 2(a). Thermal stability for layer-2 was approximately 350 °C with slight decomposition weight loss of >5 %, and then for layer-3, curve shifting towards the right side shows that thermal stability was good enough for the same with negligible decomposition weight loss of >2 %, and the thermal stability this was 355 °C. However for layer-4 the thermal stability got reduce, the reasons are attributed that, there might be poor miscibility of polymers or there might be insufficient resin to wet the entire resin, due to this there is possibility of formation of voids makes the matrix fast decomposition of the fiber. From the earlier researcher were observed the similar phenomenon [21,23].

Variation of glass transition temperature with respect to the temperature are shown in the Fig. 2(b), layers,2,3, and 4 glass transition temperature was increased cumulatively and it was observed from the figure that layer-4.



**Figure. 2.** (a) TGA and (b) DSC Curves for different layers of laminated blended composites.

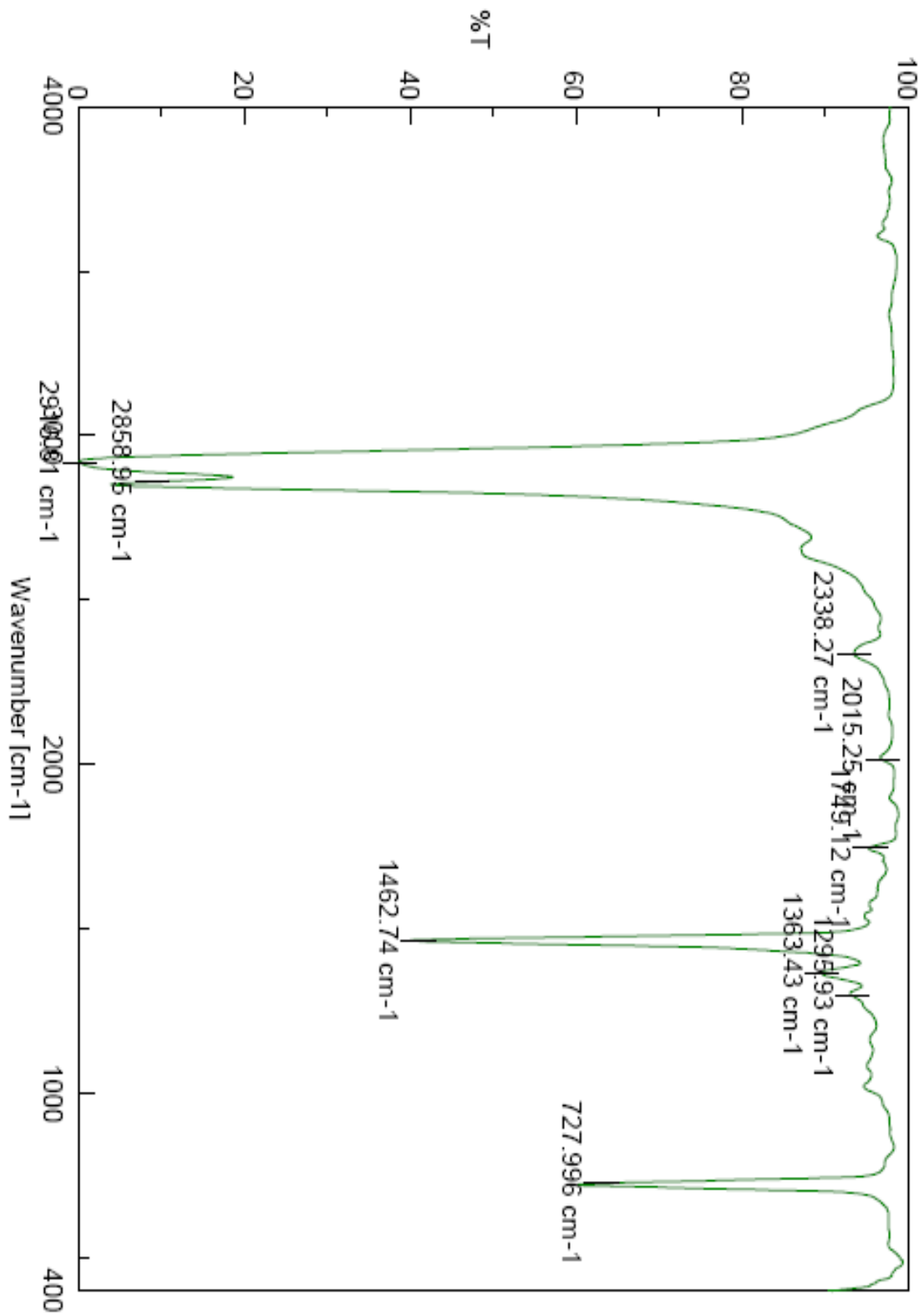


**Figure 2(continue).** (a) TGA and (b) DSC Curves for different layers of laminated blended composites.

The effect of the used fiber on crystallinity of blended composite was analyzed by DSC depicts DSC thermograms at 50-500 °C region of the second cooling cycle for pure blended composite (layer-2, 3 and 4) and blended composite including. Crystallization exothermic appears as a single, distinct peak in both cases and the Tg temperature is almost unchanged (300 °C for neat blended composite and 300 °C and 299 °C for layer-2 and 3 respectively). Thus, it seems that the fiber used in our study is active in sense of nucleation effect, probably due to the facts that (1) the average particle size of the used fiber was relatively high (2 μm), and (2) the fiber filaments were surface treated to increase the surface energy.

Fig. 3 (a) shows the variation transmittance with respect to the wave length (FTIR) analyses for (a) Layer-4 and (b) Layer-3 laminated blended composites. In Fig. 3a, we can see that the broad peak at 2958-2858  $\text{cm}^{-1}$  is attributed to stretching vibration of -OH of carboxyl groups. And the shoulder peak appeared at 1,468  $\text{cm}^{-1}$  was attributed to carbonyl stretching vibration of -COOH groups. These features revealed the existence of carboxyl groups on nanoclay molecular chains.

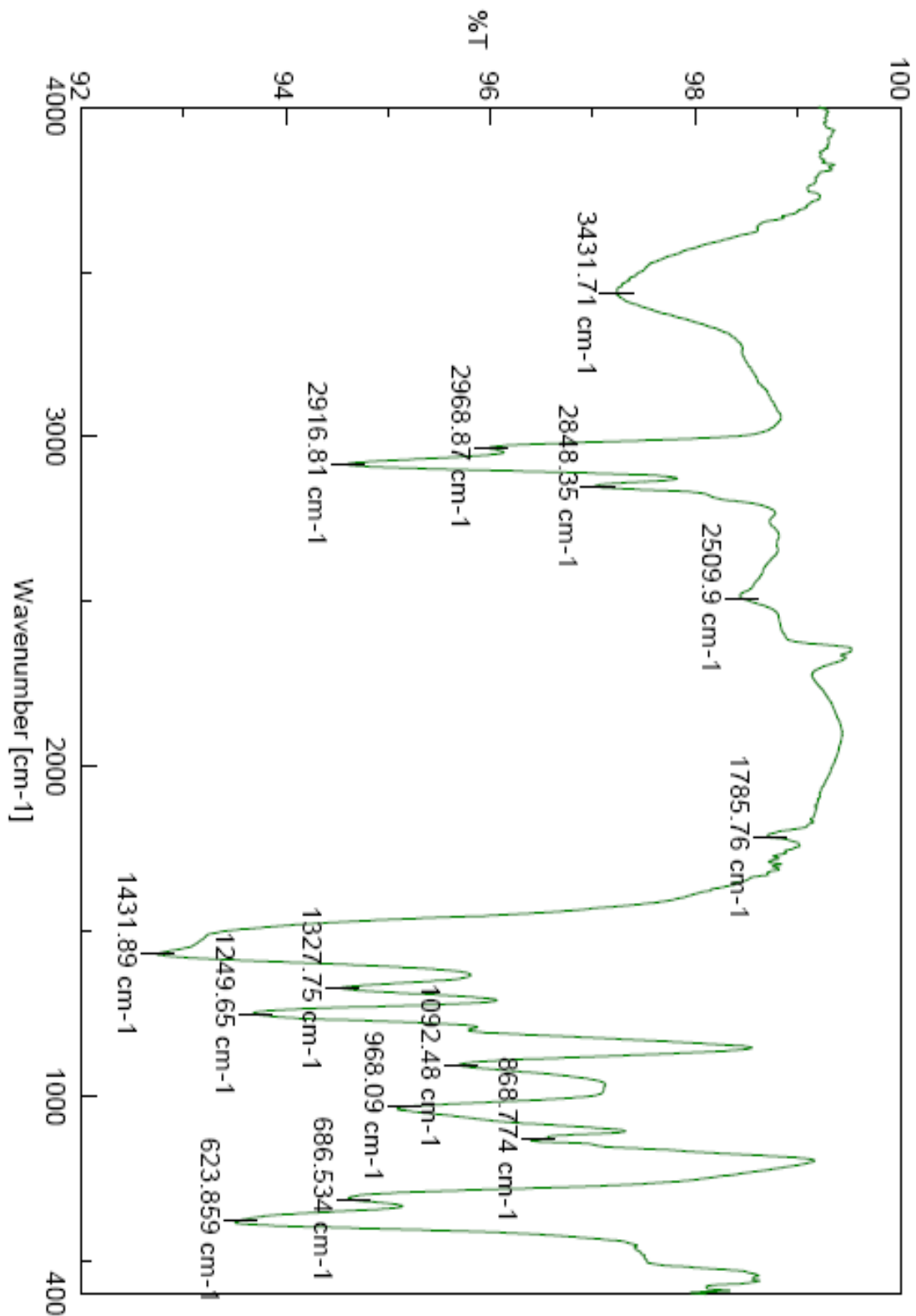
In Fig. 3b, it can be found that the characteristic peaks of blend still exist at 2916  $\text{cm}^{-1}$  and  $\text{cm}^{-1}$  for C=O and C-O-C stretching vibration, respectively. Meanwhile, the 3431  $\text{cm}^{-1}$  for the C≡N of Nanoclay particles also appeared in the layer-4 laminated composites. Especially, the hydroxyl stretching vibration of blend shifts from 3,431 to 3,421  $\text{cm}^{-1}$  for the composite with layer-4. Table 2 shows the effect of some acids, alkalis, and solvents, that is, glacial acetic acid, nitric acid, hydrochloric acid, ammonium hydroxide, aqueous sodium carbonate, aqueous sodium hydroxide, carbon tetrachloride, benzene, distilled water, and toluene were used on the matrix and the hybrid composites were studied.



(a)

**Figure 3.** FTIR analyses for (a) Layer-4 and (b) Layer-3 laminated blended composites.





(b)

**Figure 3(continue).** FTIR analyses for (a) Layer-4 and (b) Layer-3 laminated blended composites.

**Table 2.** Chemical resistance of polyester and vinylester blend laminated composites of different layers.

Chemical resistance	Layer-0	Layer-1	Layer-2	Layer-3	Layer-4
Hydrochloric acid	0.859	0.875	0.850	0.845	1.452
Acetic acid	0.235	0.236	0.230	0.214	0.485
Nitric acid	1.532	1.534	1.541	1.520	1.78
Sodium hydroxide	0.523	0.254	0.251	0.246	0.356
Sodium carbonate	0.231	0.230	0.221	0.220	0.256
Ammonium hydroxide	0.742	0.741	0.740	0.742	0.765
Benzene	10.14	9.454	9.452	9.256	9.325
Toluene	-4.85	-3.994	-3.951	-3.489	-5.687
Carbon tetrachloride	2.59	2.424	2.410	2.405	2.965
Distilled water	1.252	1.242	1.230	1.265	2.365

It was clearly evident that weight gain is observed for almost all the chemical reagents except toluene. It is also observed from the table that layer-4 gain more weight than other laminates. The reason is attack of the carbonated hydrocarbons on the cross-linked blended system. The positive values indicate that the laminates were swollen with gel formation rather than dissolving in chemical reagents. It was further observed that laminates were also resistant to water.

#### 4. CONCLUSIONS

The experimental investigations used for the analysis of tensile behavior of bi-woven aramidic fiber reinforced polymer laminates leads to the following conclusions. The laminated specimens with lesser thickness lead to more ultimate tensile strength irrespective fiber orientations. Young's modulus of specimens increases with increase in laminates irrespective its orientation. Flexural strength and tensile strength were improved up to layer-3 but decreases after wards, however, flexural modulus and tensile modulus were increased linearly up to layer-4. Similarly chemical resistance and FTIR results were also good for the composites.

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