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Comparative Study of Blends of Polyvinyl Chloride/Poly Methyl-methacrylate and Polystyrene/Poly Methyl-methacrylate using Density, Viscometry and FTIR Methods

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Abstract: *Polyvinyl chloride, poly (methacrylate) and Polystyrene are frequently use polymers but in considering the chemical and physical properties, some of them suffer from mechanical and other failures such as instability, rigidity, and non-biodegradability etc. This study is aimed investigating the compatibility of various blends of polyvinyl versus poly (methyl methacrylate) as well as blends from polystyrene and poly (methyl methacrylate) (in chloroform solvent) using density, viscometry and Fourier transformed infra-red spectroscopy methods. The results obtained indicated that PV/PMMA blends have good degree of compatibility while PS/PMMA blends did not show any observable compatibility.*

Key Words: *Comparative, blends, polyvinyl chloride, poly (methylmethacrylate), polystyrene, density, viscometry, FTIR.*

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List of symbols and abbreviation

PMMA	poly (methyl methacrylate)
PS	polystyrene
PVC	poly (vinyl chloride)
FTIR	Fourier Transform Infrared Resonance
[Ƞ]	intrinsic viscosity
Ƞrel	relative viscosity
Ƞsp	specific viscosity
C	concentration
K'	Huggins's coefficient
K"	Kraemer's coefficient
x	Mark-Houwink exponent
t	flow rate of the solution blend
t_o	flow rate of the solvent (chloroform)

1.0 Introduction

Polymer blends have become a very important subject for scientific investigation in recent years because the blend tend to exhibit properties that maybe more desirable than either of its components and hence, they receive better commercial acceptance. Blending combine's polymers to produce new ones with improve materials properties and achievement of reduced research and development expenses compared to the development of new monomers and polymers to yield a similar property profile (Robeson, 2007). Blends offer a major alternative in solving emerging application requirements in engineering and other specialized fields. Therefore, a study on compatibility of polymer has industrial and academic significant. This is because blending leads to polymers with better and desirable properties that would be widely accepted in the industries for the production of polymeric materials with specific applications through an inexpensive route which may not be achievable by either of the pure polymers that constituted the blend (Oh and Kim, 1999). The enhanced activities of polymer blends have been utilized in the production of advanced high-performance polymeric materials, which has also open up the need for basic knowledge on their phase behavior (Oh and Kim, 1999). Literature reveals that blending is only possible when the polymers are compatible (Hirotsu, *et al,* 2000). Compatibility of polymer blends is basically influenced by various factors including intermolecular interaction, morphology, crystalline phase, and surface tension (Al-Rawajfeh *et al*. 2005). However, the degree of compatibility is strongly dependent on very much dependent over the interaction between the polymeric phases of the blends (Hirotsu, *et al*., 2000). Most of the published works on polymer blends were more of academic than industrial based researches but in recent times blending has been accepted an effective method for designing polymer materials with various properties through adjustment of properties of the base polymers without the development of the new macromolecules whose desirability might not been adequately met compared to the blend products. Successfully polymer blending has been achieved by blending with different synthetic and natural polymers. For example, Visakh, *et al*. (2013) reported on the use of cellulose, chitin, starch, soy protein, casein, hemicelluloses, alginates, polylactic acid and polyhydroxyalkanoates to produce several blends, nanocomposites and nanocomposite-based polymers. Properties of the blended products were unique and differ from those of the pure polymers. Li *et al*., (2005) found that blending of synthetic biodegradable polymer, poly (lactic-co-glycolic acid) (PLGA) and natural proteins, gelatin (denatured collagen) and elastin led to the production of excellent scaffold for tissue engineering. The blend product displayed better properties than the pure polymers. Ghaffar *et al*. (2019) found that the tensile strength, thermal strength and other properties of low-density polyethylene were improved by blending with some natural polymers including rubber, starch, and lactic acid.

In view of several positive results obtained through polymer blending, the need for continuous researches on ways of improving functional properties of traditional, biodegradability and versatile plastics such as poly (vinyl chloride) polystyrene and poly (methyl methacrylate) is essential. Hence the present study is aimed at blending those using density, viscometry and FTIR measurements. These methods are quick and simple for compatibility studies in polymer blends because they require no expensive equipment and yet offer a classification of the blends into compatible or incompatible (Oh and Kim, 1999).

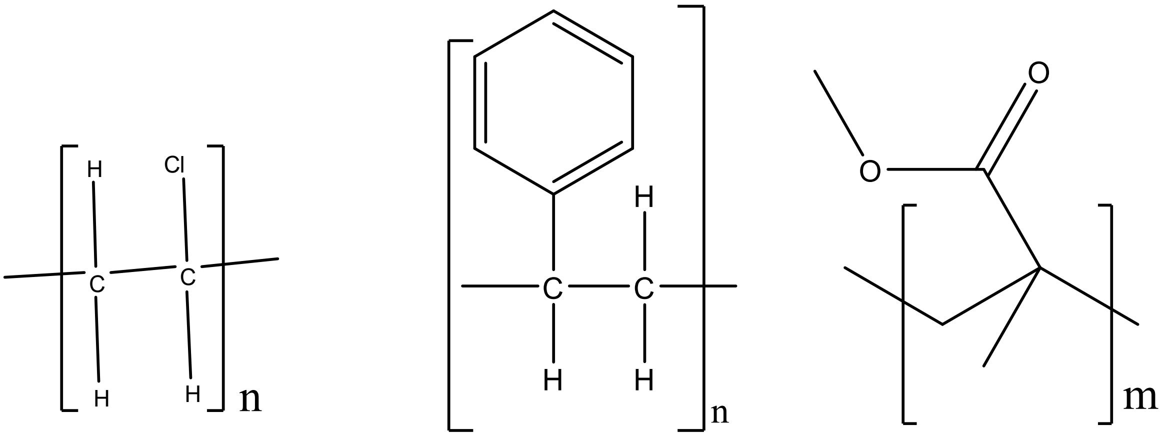
Polyvinyl chloride is one of the versatile and third most widely used synthetic plastics that are among the largest volume commodity thermoplastics**.** The polymer is a white, brittle solid, but can be plasticized to make it more flexible, in order to produce low cost, very durable, light weight and non-corrosive material, in that it doesn't rot, weather resistant and retains its shape at room temperature. At a very high temperature, PVC can be reshaped which means it has great recycling possibilities ((See Fig. 1). On the other hand, polystyrene (PS) is the most widely used plastics and it is an aromatic hydrocarbon polymer that is synthesized from styrene monomer (See Fig. 2). The polymer is hard, brittle and has a poor barrier to oxygen and water vapour. It is chemically inert and resistant to acids and bases but soluble in many organic solvents and is inexpensive. Some of these properties sometimes limit its applications. Consequently, blending, if feasible can enhance the useful properties of these materials. In spite of their excellent properties and applications and a large numbers of polymer blends that have been studied. Poly (methyl methacrylate) is one of the well-known brittle materials and it is among other commercially important vinyl polymers. It is a thermoplastic polymer and is widely used because of its excellent properties but commercial grade PMMA is an amorphous polymer of moderate. PMMA is an economical alternative to polycarbonate (PC) when extreme strength is not necessary (Fig. 2). However, non modified PMMA are known to be brittle, thereby limiting their usage, blending with another polymer can enhance some of the needed properties based on area of its applications. In spite of their excellent properties and applications, a large numbers of polymer blends that have been studied, literature is scanty on these polymer blends. Perhaps those to the best of our knowledge, are the two reported by Khan *et al*., (2008) and Baraka et al. (2003) using a different solvent from the one we are using. Therefore, the aim of this study is to study and compare the compatibility of these various proportions of PVC/PMMA and PS/PMMA blends.

2.0 Materials and Methods

2.1 Materials and equipment

Apparatus and equipment used in the study were weighing balance, 25 ml volumetric flasks, 250 ml conical flask, 5 ml graduated pipette, 25 ml specific gravity bottle, Oswald capillary viscometer (model 1-7), stirrer, Cotton wool, Fourier transform infrared spectrophotometer (Scimadzu FTIR-8400S), Oswald viscometer (type D), polystyrene (BDH England), poly (vinyl chloride)(BDH England), poly (methylmethacrylate) (BDH England) and chloroform (Analar BDH England), purchased from Romptech Scientific Supplies Company, Zaria.

Fig. 1: Snapshots of (a) poly (vinyl chloride) (b) polystyrene and (c) poly (methyl-methacrylate



(a) PVC (b) PS (c) PMMA

Fig. 2: Chemical structures of (a) poly (vinyl chloride) (b) polystyrene and (c) poly (methyl-methacrylate)

The composition of PVC/PMMA and PS/PMMA blends used for the compatibility study are indicated in Table 1 and 2 respectively. They were combined such that the sum of the combination is 100 or the sum of blend ratio was unity.

Table 1: Composition (%) of PVC/PMMA blends.

Blend	**PVC/PMMA**
A1	0:100

A2	10:90
A3	20:80
A4	30:70
A5	40:60
A6	50:50
A7	60:40
A8	70:30
A9	80:20
A10	90:10
A11	100:0

Table 2: Composition (%) of PS/PMMA blends.

Blend	PS/PMMA
B1	0:100
B2	10:90
B3	20:80
B4	30:70
B5	40:60
B6	50:50
B7	60:40
B8	70:30
B9	80:20
B10	90:10
B11	100:0

2.2 *Preparation of PVC/PMMA and PS/PMMA blends*

Composition of PVC/PMMA and PS/PMMA blends prepared for this study was as recorded in Tables 1and 2 respectively. The required proportion of the blends was prepared using chloroform as a solvent. The volume prepared in each case was 100 ml. they were preserved and used for density and viscometry studies.

2.3 *Determination of density of the blend solutions*

The blend solutions density was measured using a standard specific density bottle at 30 ^{0}C with the help of digital analytical balance (Model xp-300, Denver instrument, USA) and expressed as percentage solubility of the polymer in the solvents according to the method by Mamza and Folaranmi (1996).

2.5 Viscometry analysis

10 ml of the prepared stock solution was transferred into Oswald capillary viscometer (model 1-17) maintained at 30 ^{0}C in a thermostatic water bath. The content in the viscometer was forced to rise above the marked bulb levels and the timer taken for the fluid to drop between the two marks was recorded and used to calculate specific, reduced and relative viscosities. Triplicate measurements were made for each set of measurements and the experiment was repeated for other test blends.

2.3 Fourier transforms infrared spectroscopic analysis

Fourier transforms infrared spectroscopy analysis of PVC, PS, PMMA and their blends (PVC/PMMA) and (PS/PMMA) were carried out using Scimadzu FTIR-8400S Fourier transform infra-red spectrophotometer. The sample was prepared in KBR and the analysis was carried out by scanning the sample through a wave number range of 400 to 4000cm^{-1}

3.0 Results and Discussion

Fig. 3 shows a plot for the variation of calculated density with various compositions of PVC/PMMA blends.

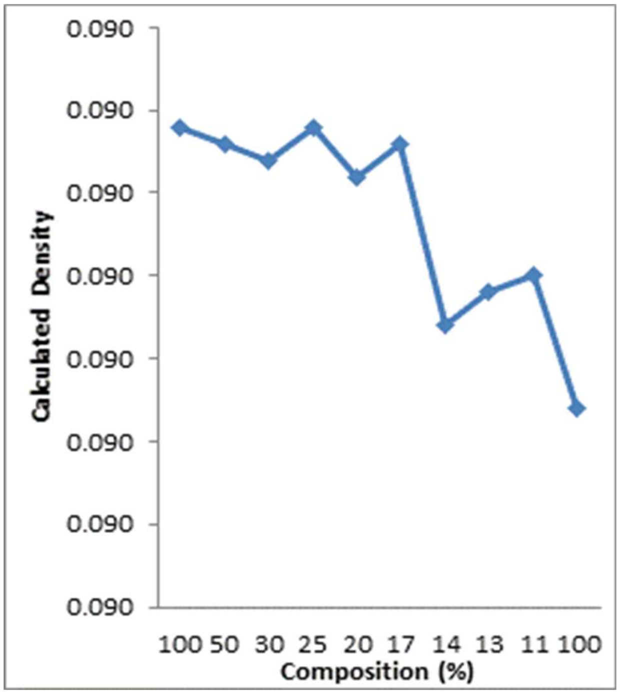


Fig. 3: Variation of density with concentration for various composition of PVC/PMMA blends

From the plot, it is evident that there is a vibrational increase in weight with composition which suggests the existent of compatibility of the blend. However, Fig. 4, which represent similar plot for PS/PMA blends depicted vibrational decrease in weight with blend composition, indicating incompatibility. Several studies have indicated that variations are in weight increase is a trend that is mostly applicable to compatible blends while weight degrease points toward incompatibility of the blend as shown for PS/PMMA blends in Fig. 8 (Chee *et al*., 2002). In PS/PMMA blends in some overlapping on most compositions (including 0.4:1.6, 0.8:1.2, 1.6:0.4 and 1.8:0.2) were observed, this can both be attributed to possible presence of incompatibility of the polymer blend at the studied temperature and solvent (chloroform).

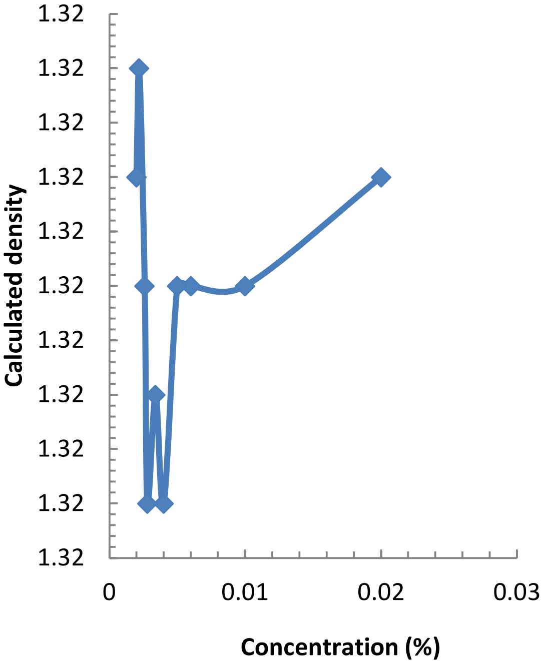


Fig. 4: Variation of density with concentration for various composition of PS/PMMA blends

3.2 Viscometric study

In viscometry, several viscosity terms can be deduced from relative viscosity measurements including specific and reduced viscosities. The relative viscosity was calculated using equation 1

$$\eta_{rel} = \frac{t}{t_0} \quad (1)$$

where t is the flow rate of solution blend, and t_0 is the flow rate for the solvent. The specific viscosity is expressed in equation 2 while equation 3 gives the expression for the reduced viscosity,

$$\eta_{sp} = \frac{t - t_0}{t_0} \quad (2)$$

$$\eta_{rel} = \frac{\eta_{rel} - 1}{C} \quad (3)$$

C is the concentration in percentage, and other parameters are as defined earlier. Figs. 5 and 6 show the variation of relative viscosity of polymer blends (PVC/PMMA & PS/PMMA) with concentration. The variation of specific viscosity with concentration of PVC/PMMA and PS/PMMA blend is presented in Figs. 7 and 8 while Figs. 9 and 10 depict the variation of specific and reduced with concentration for PVC/PMMA and PS/PMMA blends respectively.

From Figs. 9, 11 and 13 respectively are plots of PVC/PMMA blends showing interaction in some certain compositions and also shown some level of linearity on the plots which are evidence of compatibility of the blends. Whereas from the plots of PS/PMMA blends in Figures 6, 8 and 10, the pattern of variation is seems to be parallel to each other (they all assume S-shape plots) indicating that they all follow the same mechanism and that blending has not created significant interaction in rheological behaviour of the polymers(incompatibility).

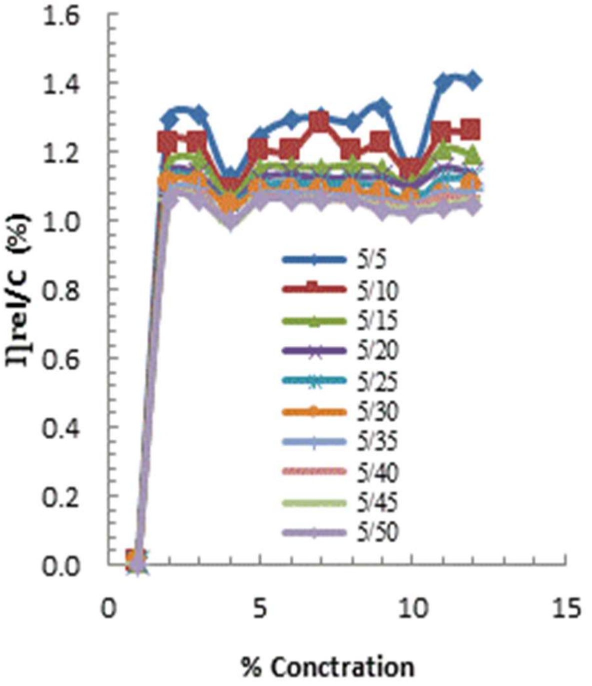


Fig. 5: Variation of relative viscosity with concentration for PVC/PMMA blends

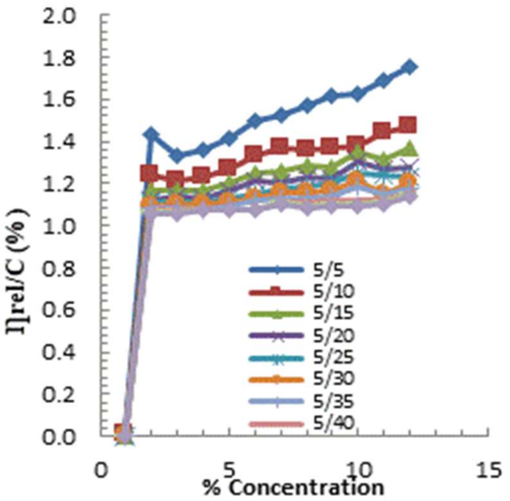


Fig. 6: Variation of relative viscosity with concentration for PS/PMMA blends

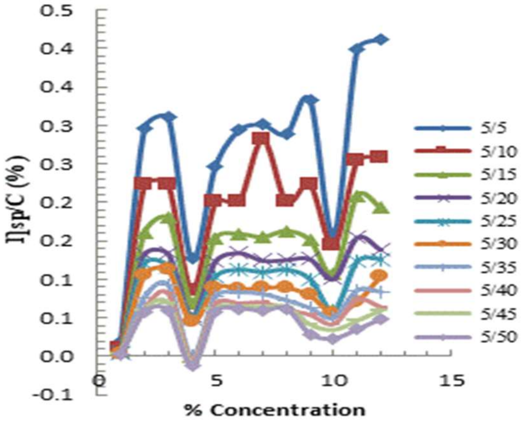


Fig. 7: Variation of specific viscosity with concentration for PVC/PMMA blends

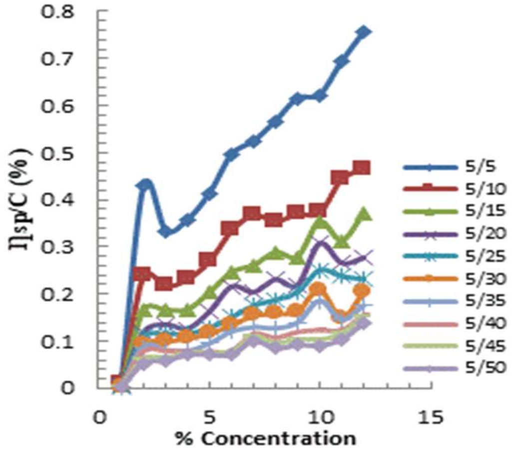


Fig. 8: Variation of specific viscosity with concentration for PS/PMMA blends

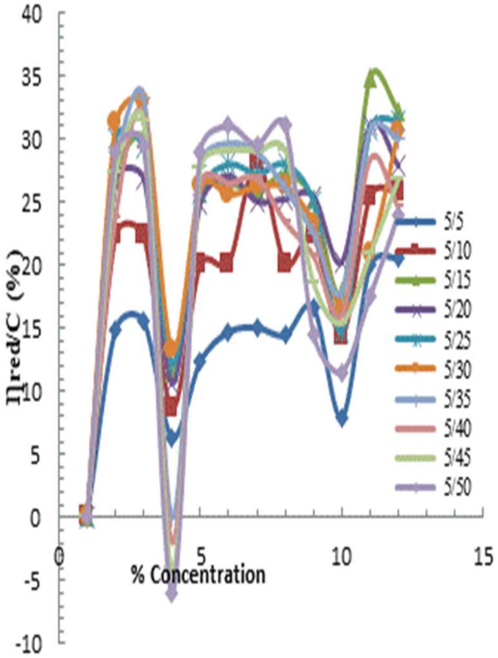


Fig. 9: Variation of reduced viscosity with concentration for PVC/PMMA blends

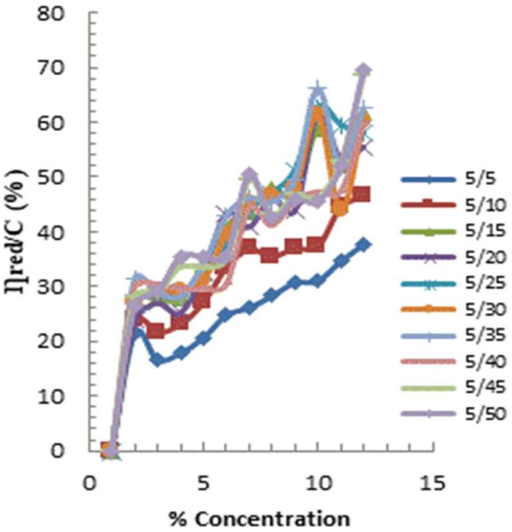


Fig. 10: Variation of reduced viscosity with concentration for PS/PMMA blends

3.1 FT-IR Analysis

FTIR spectrum in Fig. 11 of 00:100 (00: 2.0 g/dl) blend of PVC: PMMA indicated absorption bands at 667.39 cm^{-1} assigned to C-Br stretch in alkyl halides. C-N stretch was found at 1030.02 cm^{-1}. The absorption band at 1163.11 cm.$^{-1}$ is due to C-H wagging mode of vibration of the – (CH_2H) bond. This spectrum is comparable to the one reported by Subban and Ar (2004).

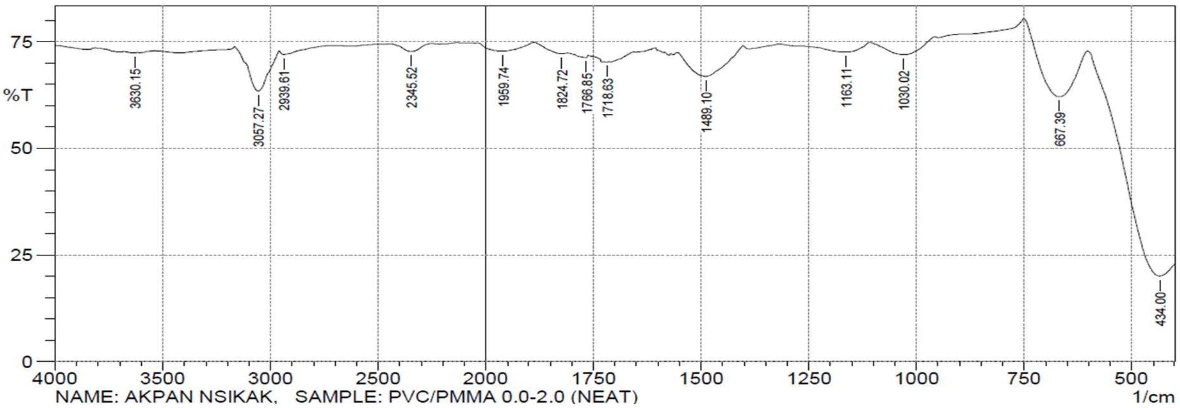


Fig. 11: FTIR spectrum graph of 00:2.0 (PVC/PMMA)

FTIR spectrum shown in Fig. 12 represent that of PVC/PMMA blend of composition, 10:90 (0.2:1.8) and it reveals the presence of –C=C-H bending vibration at 673.18 cm^{-1} and a peak due to C-H stretching ~~r~~at 1035.81 cm^{-1}, whereas, =C-H stretching displayed absorption peaks at 3036.06 and 3090.07 cm^{-1}. Absorption peak due to O-H stretch was observed at 3466.2 cm^{-1}.

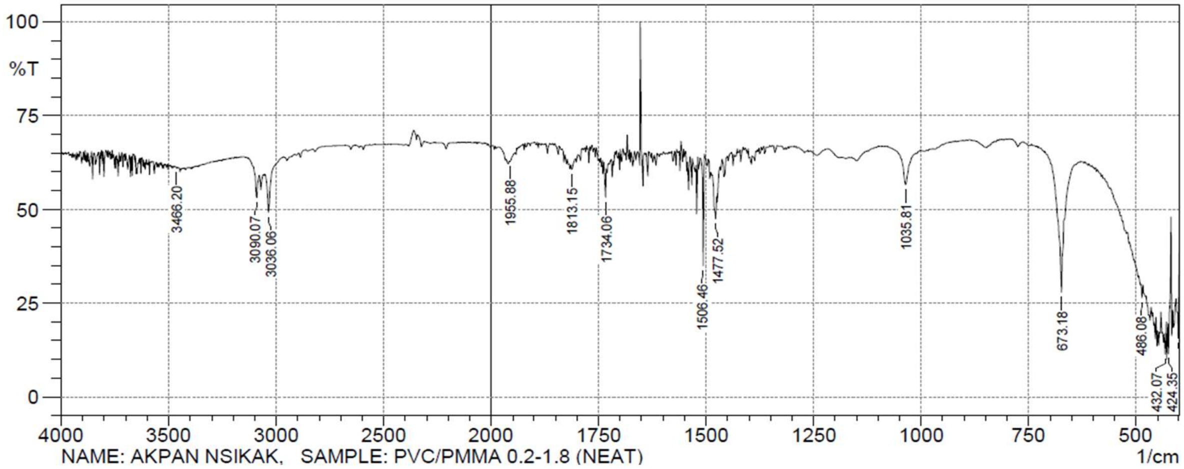


Fig. 12: FTIR spectrum graph of 02:1.8.0 (PVC/PMMA)

The FTIR spectrum of 20:80 (0.4:1.6) composition of PVC/PMMA is shown in Fig. 13. The spectrum indicated the presence of –C=C- and =C-H stretches at 1647.26 cm^{-1} and 3090.07 cm^{-1} respectively while symmetric stretching mode due to N-O bending was observed at 1506.46 cm^{-1}~~.~~ The absorption band at 673.18 cm^{-1} was assigned to –C=C-H vibration. Other stretching modes of vibration observed at 3036.06, 1730.2 and 11477.52 cm^{-1} are attributed to C-H, C=O and C-C stretches respectively.

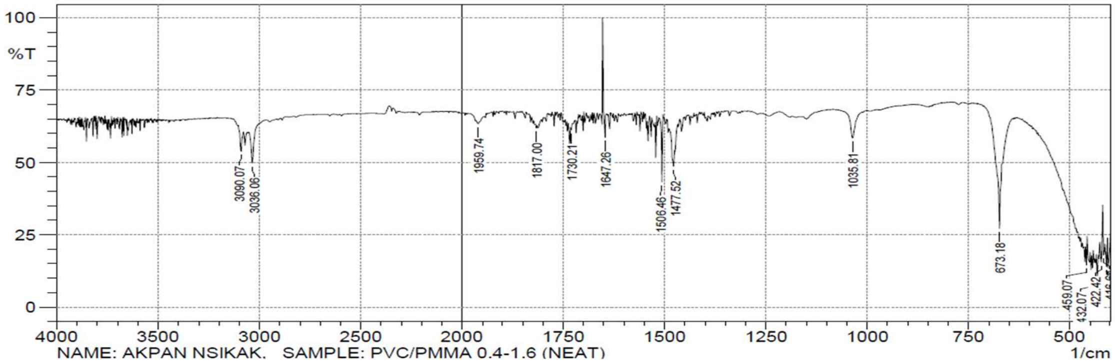


Fig. 13: FTIR spectrum graph of 0.4:1.6 (PVC/PMM

FTIR spectrum in Fig. 14 shows the various functional groups that were native for of 30:70 (0.6:1.4) compositions of PVC/PMMA blends. The spectrum indicated two =C-H stretching due to alkenes at 3036.06 and 3090.07 cm^{-1} respectively. Two normal stretching mode of vibration observed at 673.18 and 1734.06 cm^{-1} were ascribed to C-Br and C=O functional groups respectively.

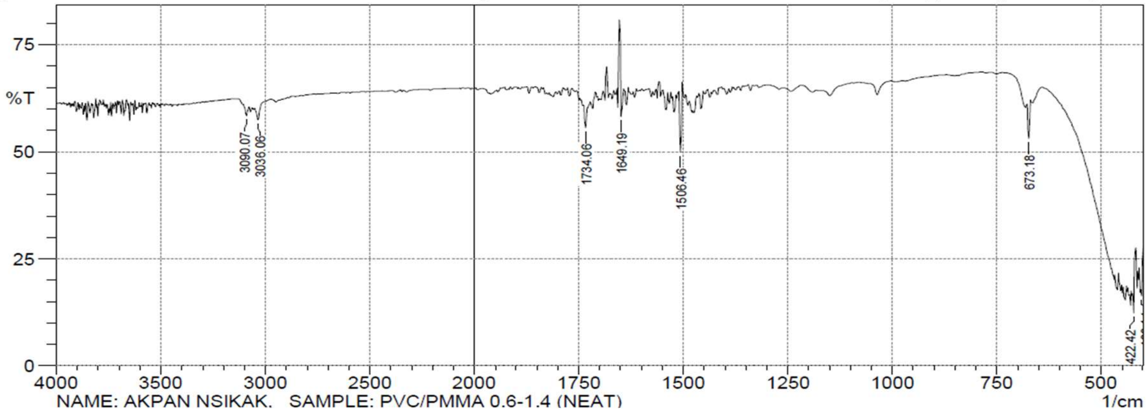


Fig. 14: FTIR spectrum graph of 0.6:1.4 (PVC/PMMA)

The FTIR spectrum of 40:60 (0.8:1.2) PVC/PMMA compositions are shown in Fig. 15, the spectrum exhibited absorption bands at 673.18 cm^{-1} and 1734.06cm^{-1} that indicates C-C aromatic stretching (in-ring). The observed at 1035.81 cm^{-1} and 1035.81 cm^{-1} represent aliphatic amines. Peaks at 1683.91 and 1734.06 cm^{-1} are consequences of C=O indicated vibration characteristic of α, β–unsaturated aldehydes and ketones. C-H stretching vibration band, characteristic of aromatics was also observed at 3036.06 cm^{-1}.

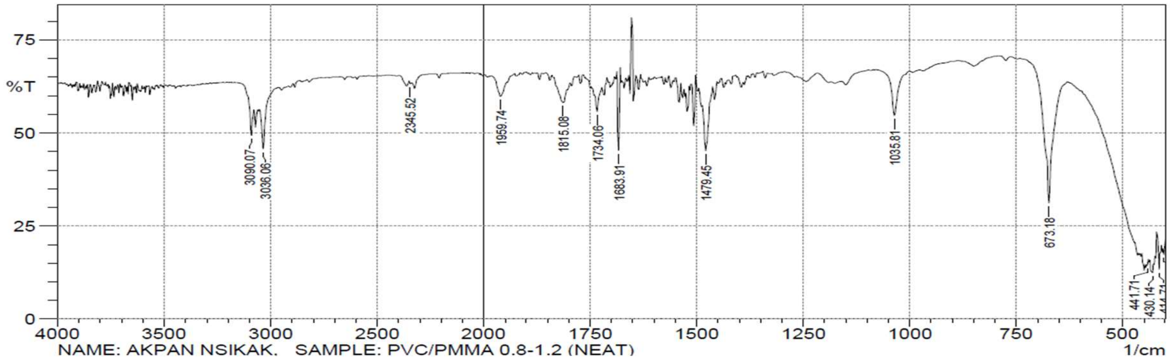


Fig.15: FTIR spectrum graph of (0.8:1.2) PVC/PMMA

FTIR spectrum of 50:50 (1.0:1.0) PVC/PMMA blends is shown in Fig.16, the spectrum shows a strong C-Br stretching at 673.18 cm^{-1}, =C-H stretching vibration at 3036.06 and 3070.78 cm^{-1} while C-C stretch was observed at 1477.52 cm^{-1} and C-N stretch at 1035.81 cm^{-1}.

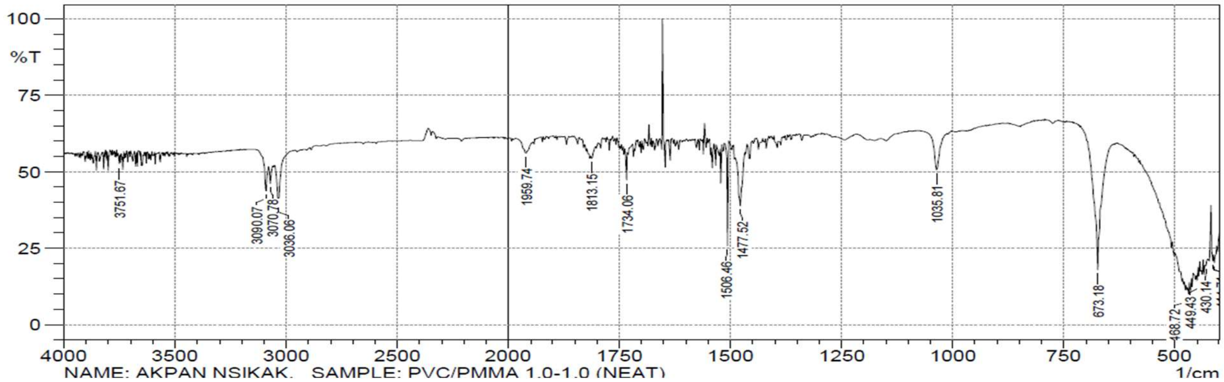


Fig.16: FTIR spectrum graph of 1.0:1.0 (PVC/PMMA)

At PVC/PMMA blend composition of 60:40 (1.2:0.8), the FTIR spectrum obtained is shown in Fig. 17. The peaks at 671.25 cm-1 indicate C-Br stretches. Peaks at 1031.95 and 1170.83 cm^{-1} indicated stretching vibration characteristic of C-N yielded frequency band at 3352.39 cm^{-1} due to $1^0,2^0$ amine and amides.

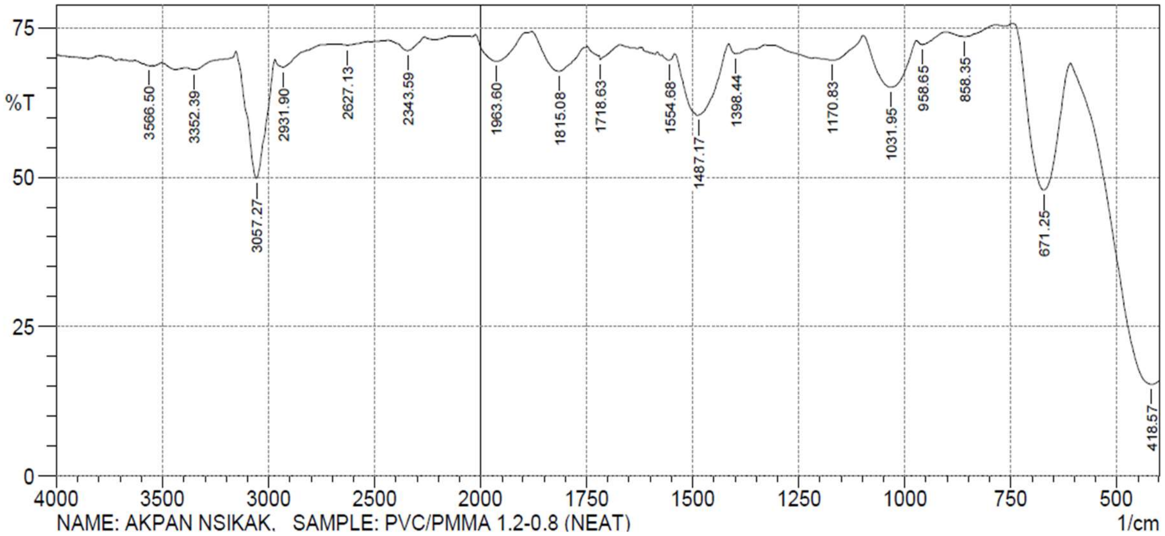


Fig. 17: FTIR spectrum graph of 1.2:0.8 (PVC/PMMA)

Recorded FTIR spectrum in Fig.18 for PVC/PMMA blend composition of 70:30 (1.4:0.6) revealed the characteristic of C-Br stretching and was observed at 673.18 cm^{-1}. At 3036.06 and 3090.07 cm^{-1} peaks obtained were due to stretching mode of vibration of =C-H bonds which reveal alkenes group. Also, frequency band at 1479.45 cm^{-1} was assigned to C-C bond stretching in aromatic ring.

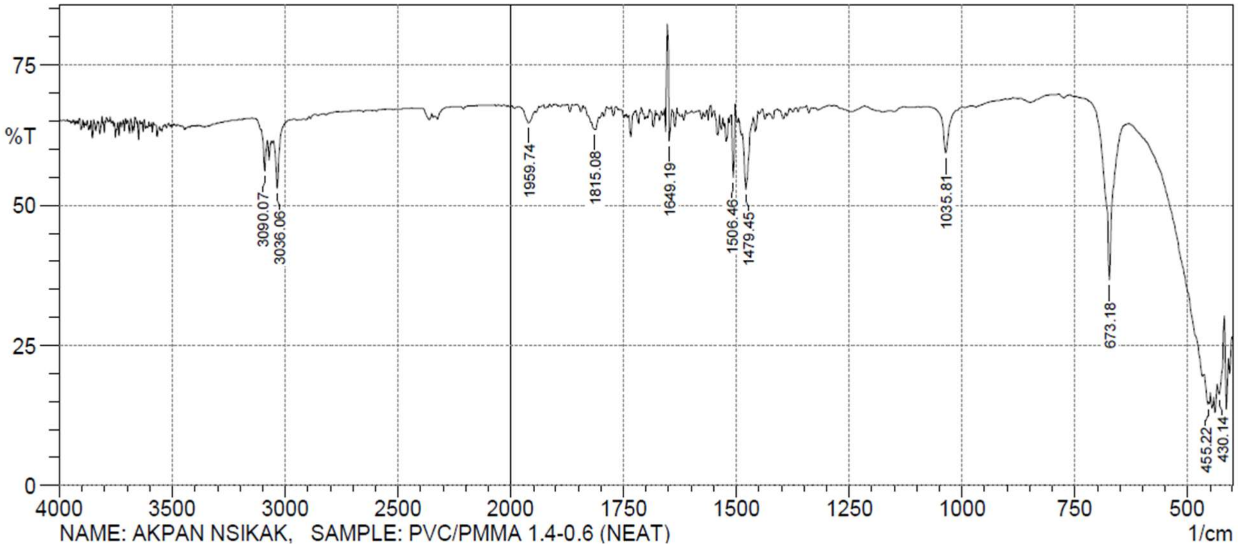


Fig. 18: FTIR spectrum graph of 00:2.0 (PVC/PMMA)

At 80:20 (1.6:0.4) PVC/PMMA blend composition, the FTIR obtained (Fig. 19) revealed the presence of C-O bond stretching (due to the presence of alcohols, carboxylic acids esters or ethers. C=O stretching shifted from 1683.91 to 1734.06 cm^{-1} revealing α, β-unsaturated aldehydes, ketones and aldehyde and unsaturated aliphatic respectively. The presence of bond stretching at 3443.05 cm^{-1} may be due to alkene =C-H bond.

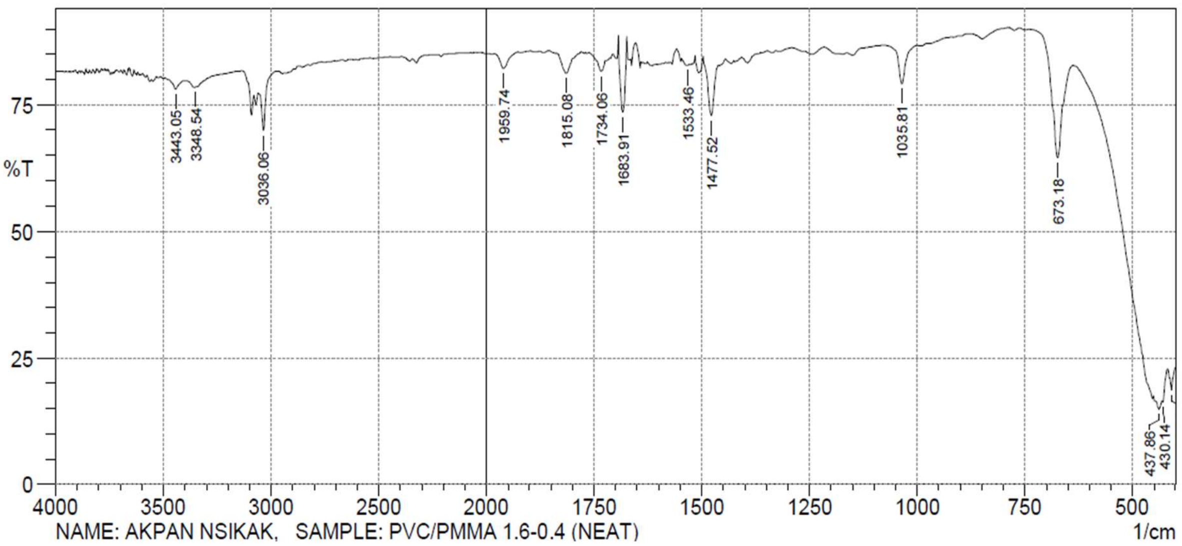


Fig. 19: FTIR spectrum graph of 1.6:0.4 (PVC/PMMA)

The FTIR spectrum in Fig. 20 reveals functional groups that are typical for PVC/PMMA blend composition of 90:10 (1.8:0.2). The spectrum contains C-Br stretching at 673.18 cm^{-1} which indicated the occurrence of alkyl halides while C=O stretching at 1683.91 and 1734.06 cm$^{-1 \text{ respectively}}$. The broad band occurring at 3036.06 cm^{-1} indicated hydroxyl group (i.e. OH stretch).

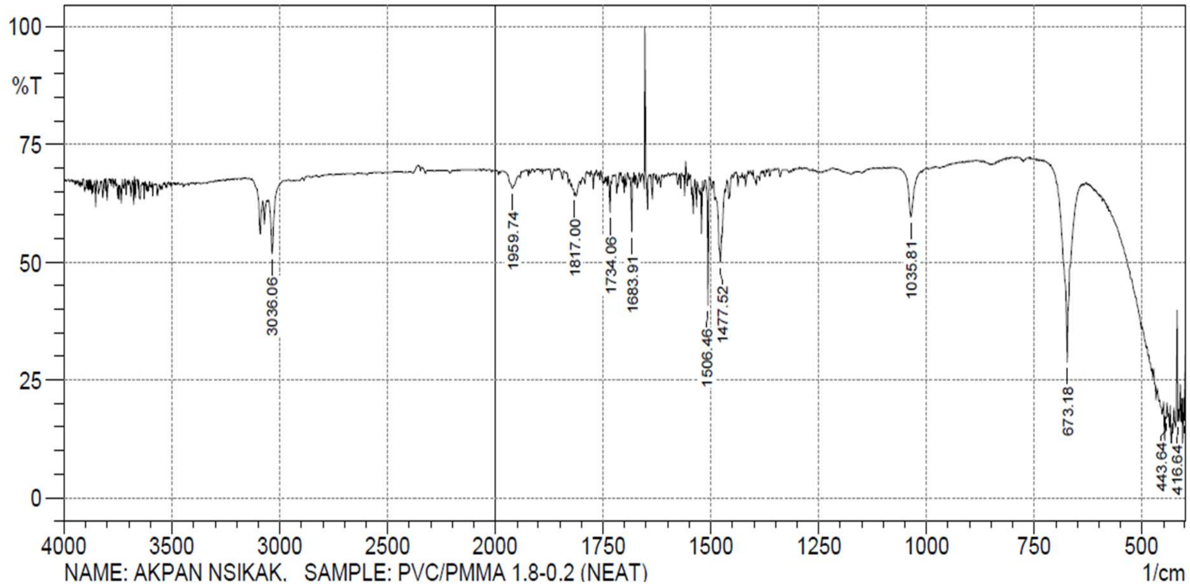


Fig. 20: FTIR spectrum graph of 1.8:0.2 (PVC/PMMA)

PVC/PMMA blends composition of 100.00 (2.0:00) exhibited FTIR spectrum shown in Fig. 21, the observed N-H bond stretching and bending were positioned at 3350.46 and 1622.19 cm.$^{-1}$ respectively. At 1473.66 cm^{-1}, C-C bond stretch in aromatic ring was also seen. Peak at 3037.99 cm^{-1} is typical for =C-H bond stretch and confirms the present of alkenes which also reveal significant interactions between PVC/PMMA. Examination of the absorption bands of each of the blends and their respective composition gave evident a shift in the frequency C=O absorption by PMMA. Therefore, there is some interaction between PVC and PMMA. Earlier reports by Saikia and Kumar (2005), pointed out that the Krigbaum seems to be well applicable in describing the compatibility of PVC/PMMA polymer blend systems.

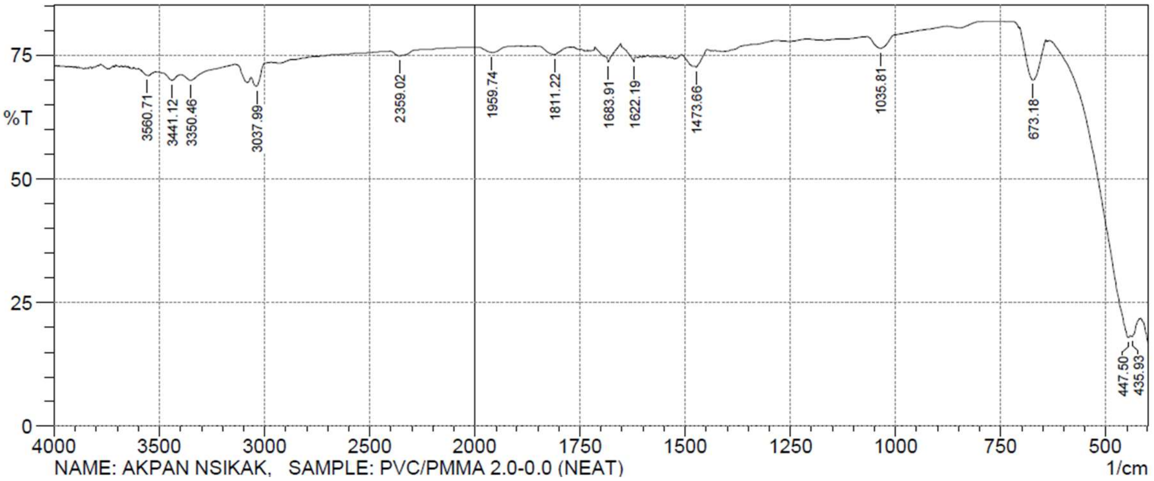


Fig. 21: FTIR spectrum graph of 2.0:0.0 (PVC/PMMA)

FTIR spectrum in Fig. 22 for 00:100 (00: 2.0 g/dl) blend of PS: PMMA indicated absorption bands at 3437.26 and at 3053.42 cm^{-1} which were assigned to O-H in carboxylic acid. Aromatic C-H stretch was found at 3053.42 cm^{1}.

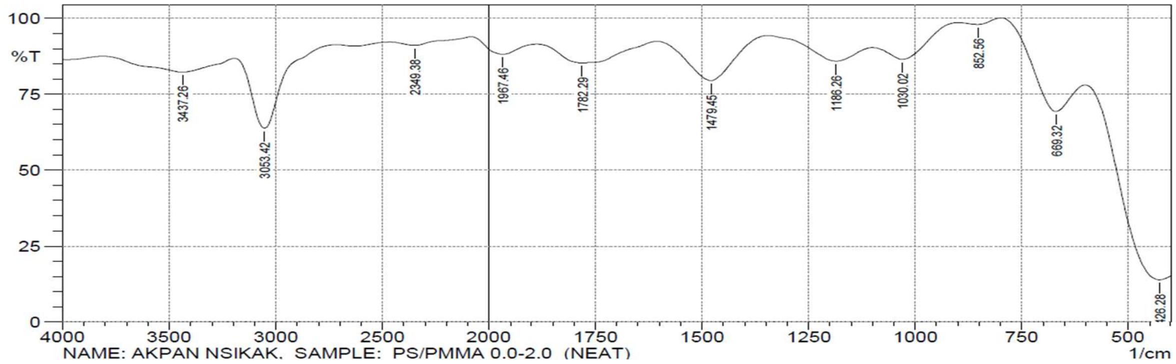


Fig. 22: FTIR spectrum graph of 0.0:2.0 (PS/PMMA)

Also, the FTIR spectrum of 10:90 (0.2:1.8) PS/PMMA blend (Fig. 23) revealed that the amide N-H and aromatic CH stretches were shifted to 3431.48 and 3049 cm^{-1} respectively. Also observed was a broad O-H stretches at 2613.63 cm^{-1} due to carboxylic acids (Vinod and Sashidhar, 2010).

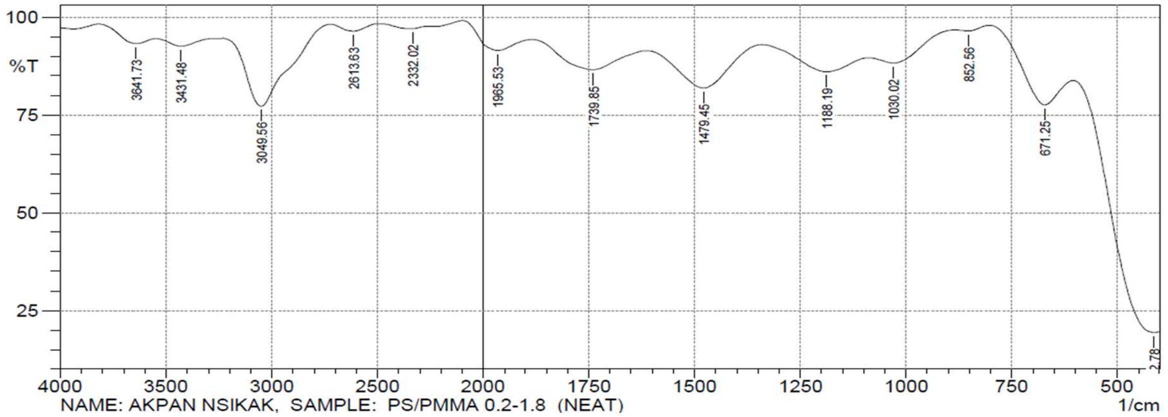


Fig. 23: FTIR spectrum graph of 0.2:1.8 (PS/PMMA)

The FTIR spectrum in Fig. 24 representing PS/PMMA blend with composition, 20:80 (0.4:1.6), indicated the presence of amides N-H and aromatic =C-H stretches which was shifted to 3429.55cm^{-1} respectively.

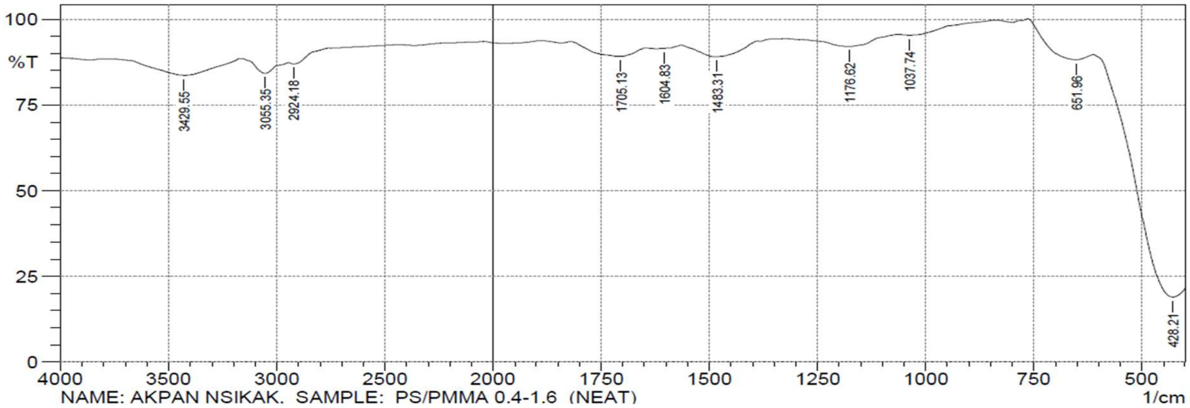


Fig. 24: FTIR spectrum graph of 0.4:1.6 (PS/PMMA)

FTIR spectrum of 30:70 (0.6:1.4) PS/PMMA blends composition (Fig. 25) indicated OH stretch due to carboxylic acid at 3435.34 cm-^{1}. Aromatic C-H stretch was observed at 3051.49 cm^{-1} indicating that the blend is aromatic.

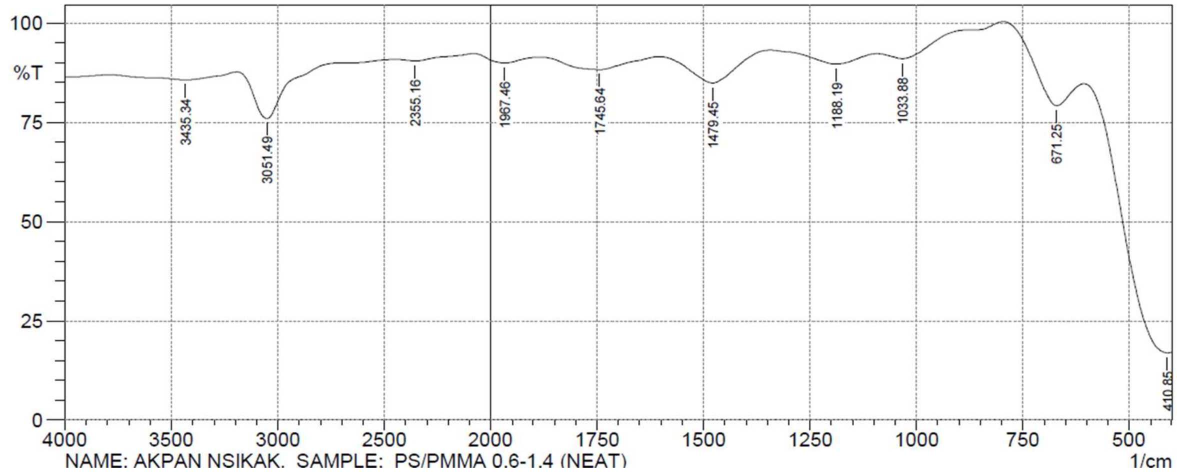


Fig.25: FTIR spectrum graph of 0.6:1.4 (PS/PMMA)

The FTIR spectrum in Fig. 26 for 40:60 (0.8:1.2) PS/PMMA composition showed absorption bands at 3437.36 and 2621.35 cm-^{1} assigned to OH stretching. (Cunha *et al*., 2007). Aromatic C-H was also found at 3055.35 cm-$^{1.}$

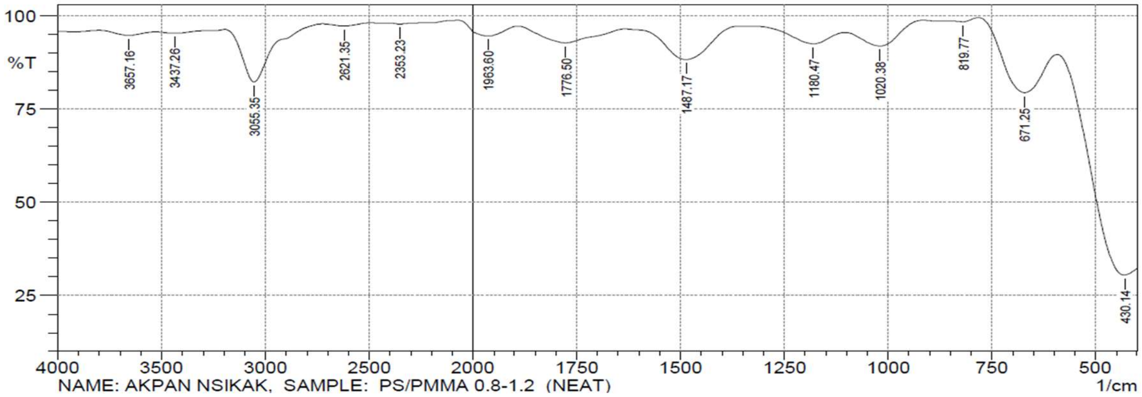


Fig. 26: FTIR spectrum graph of 0.8:1.2 (PS/PMMA)

FTIR spectrum in Fig. 27 for 50: 50 (1.0:1.0) PS/PMMA blends indicated the presence of a broad absorption band due to alkane/alkyl CH at 2935.76 cm-^{1}.

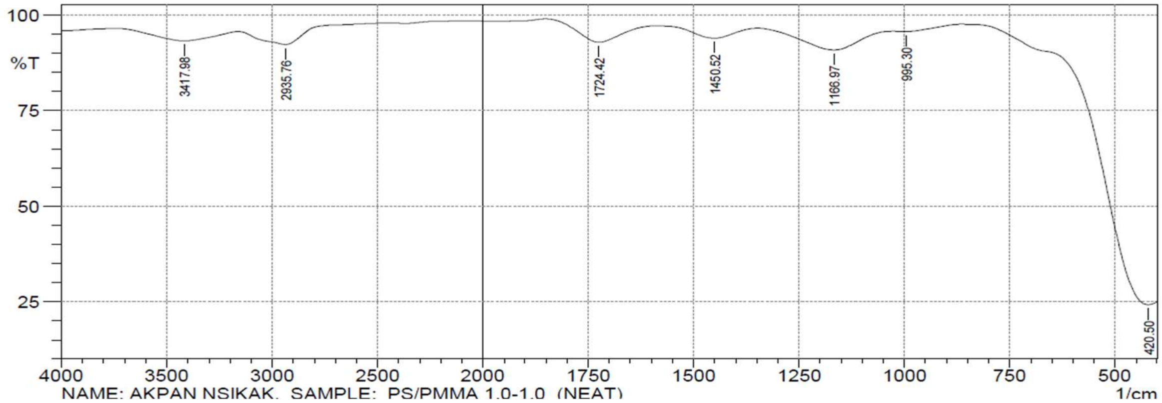


Fig. 27: FTIR spectrum graph of 1.0:1.0 (PS/PMMA)

At PS/PMMA blend composition of 60:40 (1.8:0.2), the FTIR spectrum in Fig. 28 indicated an absorption band due to OH stretch at 3406.40 cm^{-1} (associated with carboxylic acid), -CH stretch due to alkene at 3041.84 cm^{-1} and alkyl C-H stretch at 2926. 11cm^{-1}.

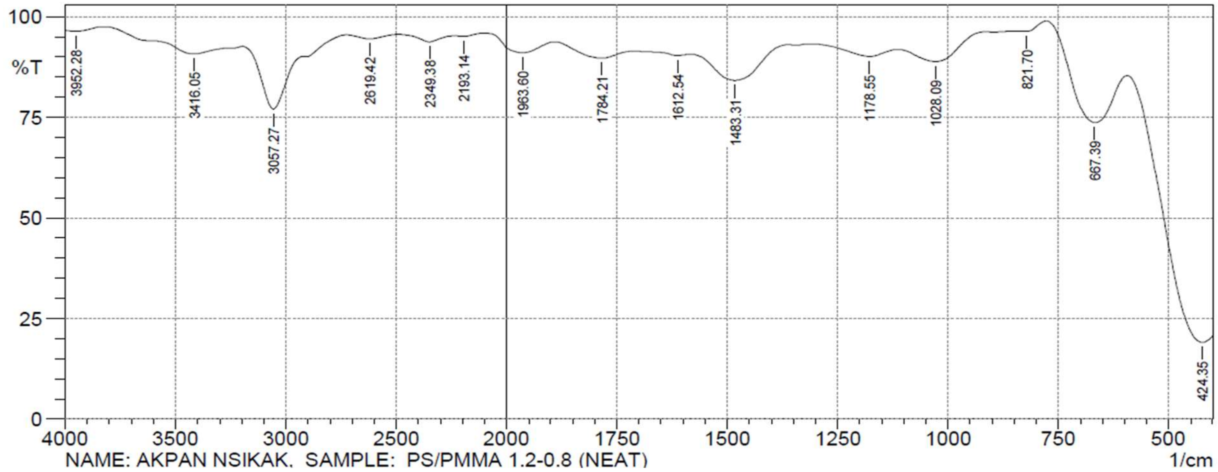


Fig. 28: FTIR spectrum graph of 1.2:0.8 (PS/PMMA)

Recorded FTIR spectrum in Fig. 29 for PS/PMMA blend composition of 70:30 (1.6:0.4) revealed the appearance of OH stretches at 3423.78 and 2621.35 cm^{-1} which signify the presence of carboxylic acid group. Aromatic C-H stretch was observed at 2055.35 cm^{-1}. Other peaks were observed at 2621. 35, 2914.54 and 2922.23 cm^{-1} and are attributed to CH stretches due to alky and alkanes respectively.

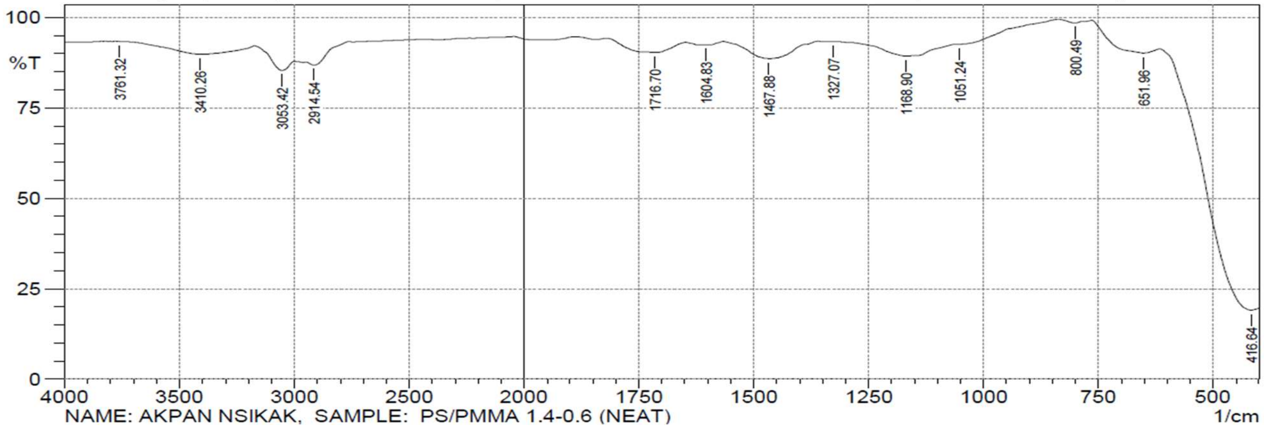


Fig. 29: FTIR spectrum graph of 1.4:0.6 (PS/PMMA)

At PS/PMMA blend composition of 80: 20 (1.4:0.6), the FTIR spectrum (Fig. 30) revealed alkanes and alkyl peaks at 2347.45 cm^{-1}. The absorption band of PS/PMMA blends reveal no significant interactions and the aromatic rings was not affected by blending.

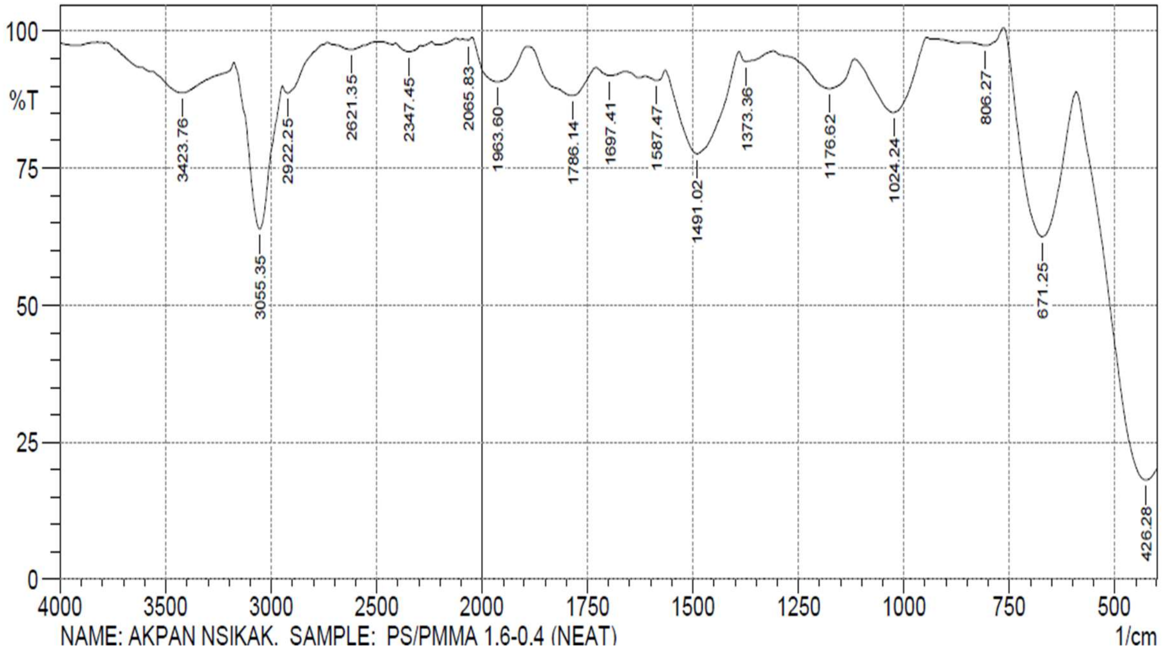


Fig. 30: FTIR spectrum graph of 1.6:0.4 (PS/PMMA)

The FTIR spectrum in Figure 31 for PS/PMMA blend composition of 90:10 (1.2:0.8) indicated C-H stretches at 2922.2cm^{-1} which portray the presence of strong aromatic group.

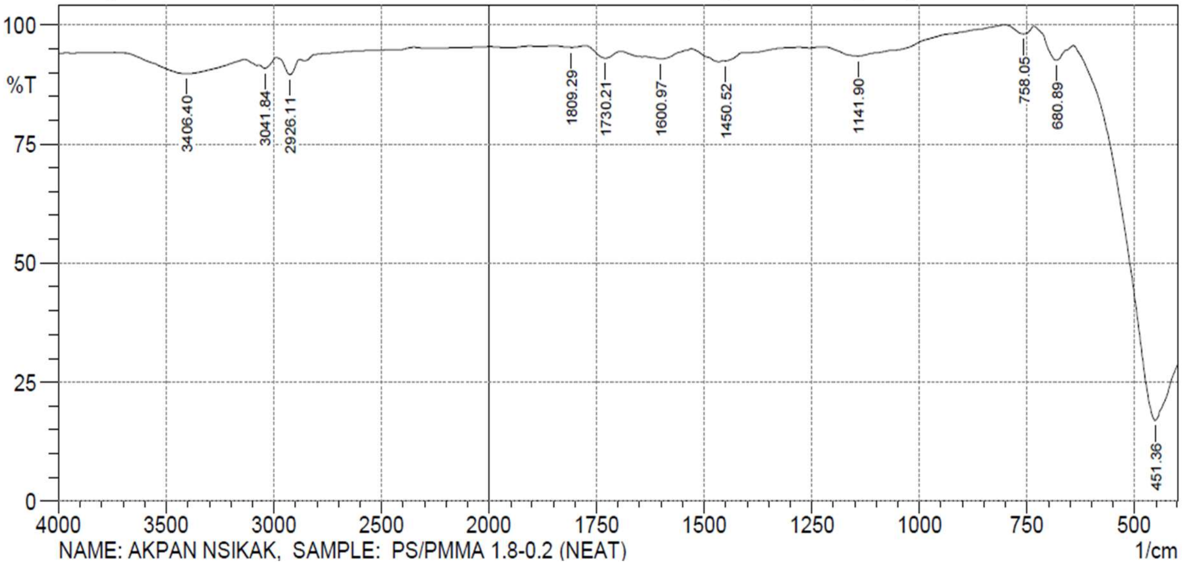


Fig.31: FTIR spectrum graph of 1.8:0.2 (PS/PMMA)

The PS/PMMA blends composition of 100.00 (2.0:00) gave FTIR spectrum shown in Fig. 32. The spectrum displayed the appearance of =C-H stretching at 3078.80 cm^{-1} and did not provide evidence of significant interactions. Consequently, PS/PMMA does not have significant compatibility at any composition which is in agreement with the work reported by Mohammad and Raina (2008).

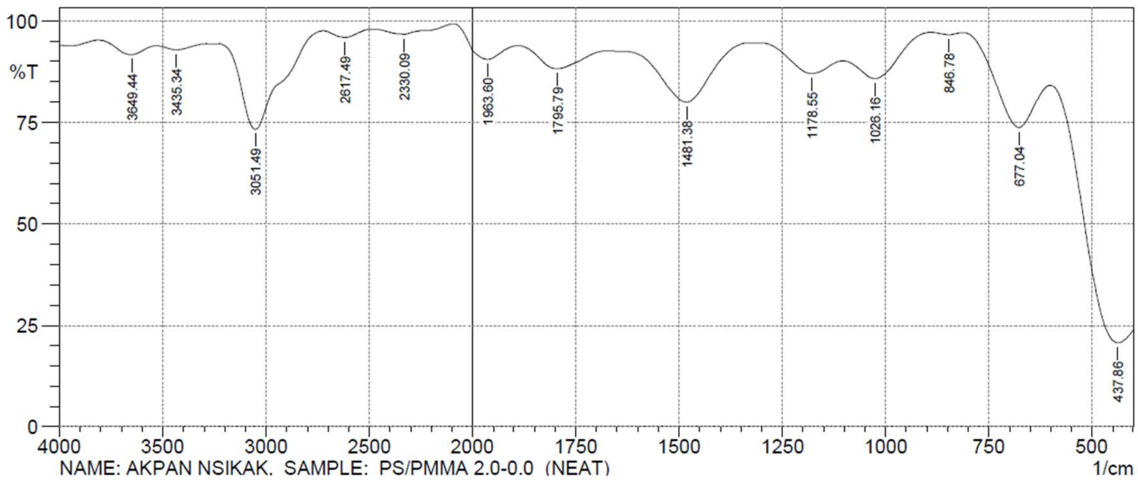


Fig. 32: FTIR spectrum graph of 2.0:0.0 (PS/PMMA

4.0 Conclusion

The FTIR techniques pointed out the existence of interaction between the carbonyl groups of PMMA and the hydrogen atom of CHCl group of PVC in the entire compositions of PVC and PMMA in both solution and solid state. However, such observable interaction was not noticeable in the spectrum of PS/PMMA blends rather the observed peaks due to PS/PMMA blends indicated no linkage in the interaction nor observable changes in the aromatic rings after blending. The three testing compatibility methods reveal that maximum interaction of PVC/PMMA blend can be obtained at 0.4:1.6, 1.6:0.4 and 0.8:1.2 compositions at 30 ^{0}C using chloroform as the solvent. Consequently, these are concentration at which the polymers can be mixed to obtain a good results, while some are of good strength and extensibility like the 1.4:0.2 blend concentration and some are of low strength and extensibility like the 1.0:1.0 concentration, but could be good based on area of applications and also indicated that increase in the PVC content enhances the toughness of PMMA/PVC blend. Testing on PS/PMMA blends shows no degree of compatibility at any compositions under similar environment compatibility was observed for PVC/PMMA blends. This may be attributed to the mutual repulsion of molecules in solutions which lead to decrease of dynamic volume of the polymer

5.0 References

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