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Preparation and Characterization of Plasticized Polymethylmethacrylate (PMMA)/Polyvinylchloride (PVC) Biodegradable Blend

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ABSTRACT

Polymethylmethacrylate (PMMA)/Polyvinylchloride (PVC) blends were prepared using a solvent casting technique. The blends were characterized using Fourier Transform Infrared Spectroscopy (FT–IR), Scanning Electron Microscopy (SEM) and biodegradation. The liquid absorption behaviours as well as the optical parameters of the prepared blends were investigated using UV- Visible spectroscopy. Optimum liquid absorption was observed in the blend that contained75% PMMA and 25% PVC, with the liquid absorption increasing from 65.09% in first day to 145% in the third day. The absorption coefficients (α) and extinction coefficient (k) of the various compositions were determined and the highest α value was observed in 50% PMMA/50% PVC blends of 3166.63α and 88.4k.

Keywords: Biodegradable, polymer blends, poly (methyl methacrylate), poly (vinyl chloride)

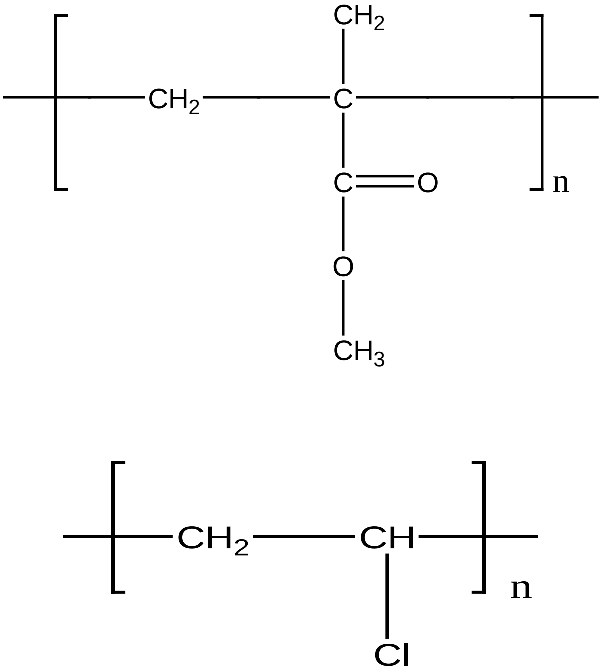
INTRODUCTON

In many decades, polymer blending makes available an abundant route to engineering of new properties in materials using accessible polymers. From Polymer blending, it is possible to produce a range of materials with properties that are superior to that of each individual component/polymers (Rhoo *et al*., 1997; Achari *et al.*, 2007; Khan *et al.*, 2008). The main advantages of the blended systems are simplicity of preparation and ease of control of physical properties by compositional changes (Acosta *et al.*, 1996; Khan *et al.*, 2008). Also it usually requires little or no extra expenditure compared to new polymer synthesis. However, the miscibility between the constituents of the polymer mixture on a molecular scale is responsible for materials with superior properties (Khan *et al.*, 2008; Al-Daeif *et al.*, 2012). Miscibility may arise from specific interactions, such as dipole-dipole forces (Khan *et al.*, 2008) and charge transfer complexes (Khan *et al.*, 2008) for homo-polymer mixtures. Segment-segment repulsion can also exist in the blends. However, due to very small entropy gain in the mixing of long chain polymers and because of the usually encountered positive heat of mixing, most polymer blends form two phases (Farhod and Mohammed, 2018). The majority of known polymeric mixtures are immiscible; however, several miscible polymer blends have been found in the last three decades (Farhod and Mohammed, 2018). There have been numerous techniques of studying the miscibility/blending of the polymeric blends (Khan *et al.*, 2008). The most useful techniques are viscometry measurements (Khan *et al.*, 2008), SEM analysis, X-ray diffraction analysis (Flora *et al.*, 2012), FT–IR (Ali *et al.*, 2009; Flora *et al.*, 2012) thermal analysis (Flora *et al.*, 2012), ultrasonic velocity measurement (Khan *et al.*, 2008), refractive index determination (Rajulu *et al.*, 1999), NMR method (Crispim *et al.*, 2000) and optical spectroscopy analysis (Achari *et al.*, 2007; Khan *et al.*, 2008; Ahmed, 2009). Various blends have been studied by several authors, including Paul and Newman (1978), Prabhu *et al.* (2013), Saleem *et al.* (2008), Ramesh *et al.* (2002), Rhoo *et al.* (1997), Belhaneche-Bensemra *et al.* (2002), Chakrabarti *et al.* (2004), and Flora *et al.* (2012). Blending provide an avenue in producing improved products with better physical, mechanical and thermal properties of the polyblends (Khan, *et al.*, 2008). A work carried out by Manuel *et al.* (2002) showed that, blend of Thin films of poly (vinyl chloride) (PVC)/poly(methylmethacrylate) (PMMA) polymer electrolytes plasticized with a combination of ethylenecarbonate (EC) and propylenecarbonate (PC) and $LiN(CF_3SO_2)_2$ as salt have been prepared by solution casting technique (Manual *et al.*, 2002). They subjected the prepared films to a.c. impedance measurements as a function of temperature ranging from 30 to 70 jC. They as well prepared PVC/PMMA composite electrolytes using TiO_2 as inorganic filler. Effect of liquid plasticizer and inorganic filler on the interfacial stability of the blend polymer electrolytes and TG-DTA analyses were included in the same study (Manual *et al.*, 2002). Critical miscibility phenomena in binary blends of a tactic, isotactic, or syndiotactic PMMA with Chlorinated polyethylene or Chlorinated PVC each with systematically varying degrees of chlorination, were reported by Khan *et al.* (2008). Because of the wider applications of plastics in various field, e.g. in agriculture and in serious waste disposal issues and pollution of the environment have been raised. However, most synthetic plastic resists microbial degradation and their polymers persist in the environment for longer time (Alabi *et al.,* 2019).A study was carried out to isolate the fungal strain having ability to adhere and degrade cellulose blended PVC films (Ali *et al*., 2009). The fungal isolate PV1 and PV2 showed adherence on the surface of the Cellulose blended PVC film. PV1 (*Phanaerochaete chrsosporium*) was more efficient than the other in degrading cellulose blended PVC films as such indicated their ability to utilize PVC as a source of nutrient. Also they revealed that, carbon dioxide production during the Sturm test indicated positive degradability test for the starch blended PVC films. The changes in the peaks of the FTIR spectra of the test samples as compared to control further explained the indication of breakdown of plastics starch blended PVC as a result of fungal treatment (Ali *et al*., 2009). A relatively small number of studies have been reported on the development of PVC/PMMA-based polymer electrolyte systems (Achari *et al.,* 2007). Therefore, the aim of this research work was to prepare PVC/PMMA blends, thus thereby plasticizing and characterizing the materials using various analytical techniques including FT–IR, SEM and UV-Visible absorption, and degradation study.

MATERIALS AND METHODS

Reagents

Polyvinylchloride (PVC) (M.wt. 93.92685g/mol; purity 99.8%; Density 1.39g/cm^3) (BDH Chemical, India) and Polymethylmethacrylate (PMMA) (M.wt. 996.000g/mol; purity 99.0%; Density 1.18g/cm^3) (BDH Chemical, England), in powder form were used as received, without further purification. Tetrahydrofuran (THF) (M.wt. 72.107 g/mol; %Purity 99.9%; Density 0.8876 g/cm^3 at 20^{o}C) (Aldon Corporation, USA) and Butanone (M.wt. 72.11g/mol; %Purity 99.70%; Density 0.799g/cm^3) (BDH Chemical, Dubai) were utilized as solvent. Plasticizer (1, 2, 3–trihydroxy propane) (M.wt. 92.10 g/mol; %Purity 99.70%; Density 1.249g/cm^3**)** (Anmol Chemicals, India), Starch (BDH Chemical, India) and distilled water were as well all used in this study.



Scheme1: Repeating Units of Polymethylmethacrylate and Polyvinylchloride

METHOD

Starch (2g) was dissolved in 40ml of distilled water on a hot plate using a magnetic stirrer, to ensure complete dissolution. 1. 13g (75%) of PMMA was dissolved in 5ml of 99.70% butanone with rigorous stirring. 1ml of the homogenous starch mixture was transferred in to a PMMA/butanone mixture 0.38g (25%) of PVC which was dissolved in 5 – 10 ml of THF (Kayyarapua, *et al.,* 2016). Upon complete dissolution the mixture was transferred to a PMMA/starch mixture, followed by the addition of 2-3 drop of propan – 1, 2, 3 – triol. This was then stirred for 15 minutes and, the resulting mixture was then cast on a clean glass plate. Upon drying, the blend was removed and stored in desiccator to avoid contact with moisture (Dixit *et al.*, 2009).Scanning electron microscopy(SEM) was carried out at 200µm magnification and 10Kv voltage which gives the optical image/surface morphology of the blends. The blends 75%PMMA/25%PVC and 50%PMMA/50%PVC were buried in soil for two weeks (Ali.*et al.*, 2009).

Liquid absorption test on the blends

Six set of blend were prepared and subjected to water absorption test. The blends were soaked for 24 Hours respectively. After each immersion, the blends were removed and wiped and then weighed and weights were noted using the formula (Manuel *et al.*, 2002; Dhakal, *et al.*, 2007; Dixit et al., 2009).

$$\text{Swelling Ratio\%} = \frac{(\mathrm{Wf} - Wi)}{Wi} 100\% \ldots\ldots..1$$

(Musa and Hameed, 2021)

Where:

Wi= Initial weight of blend before immersion in water and

W_f = Weight of blend after immersion in water

RESULT AND DISCUSSION

Infrared (IR) Analysis

The FT – IR analysis results from test carried out on the PVC, PMMA and the PMMA/PVC blends are shown in Figures 1, 2, and 3. The IR analysis gives information about the type of functional group present in a sample (Kuma and Kuma, 2013).

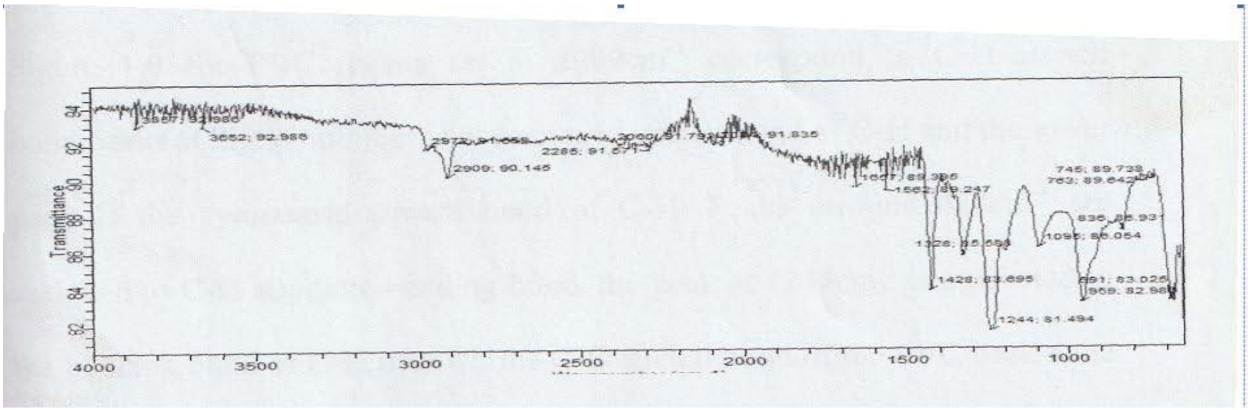


Figure1: FT-IR of polyvinylchloride (PVC) before blending

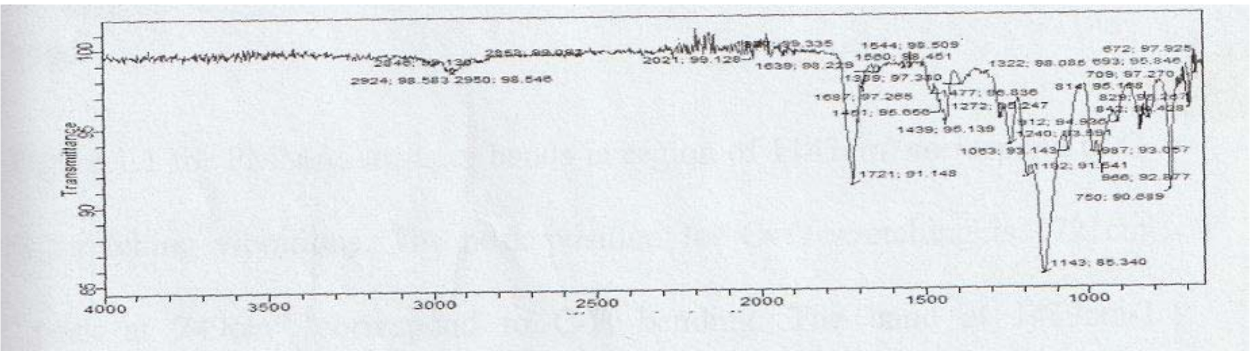


Figure 2: FT-IR spectrum of PMMA before blending

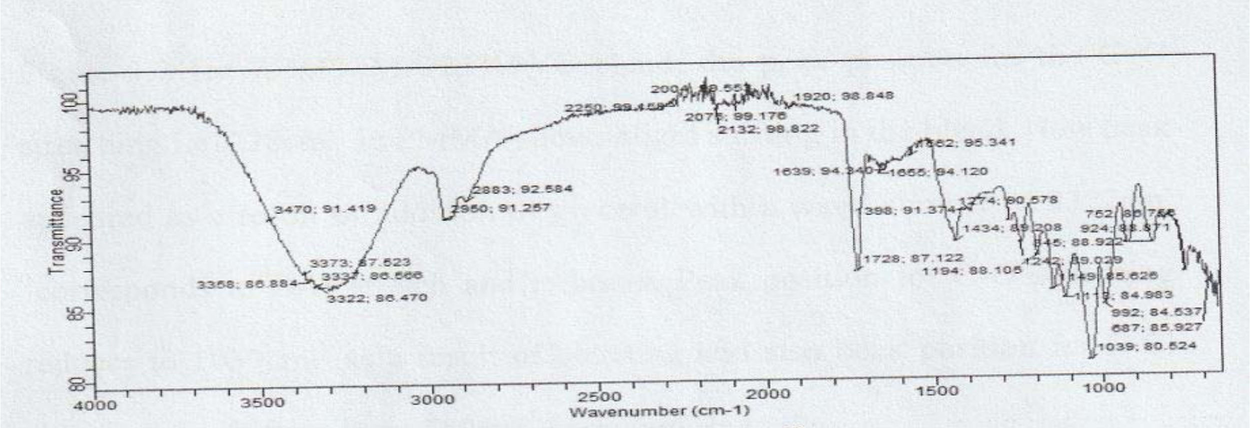


Figure 3: FR-IR spectrum of PMMA/PVC blend

Figure 1 represents the spectra for PVC, with peaks appear at 2909cm^{-1} correspond to C- H bond stretch. The peak at higher number (2910cm^{-1}) is asymmetric stretch bond of C-H and the lower peak is the symmetric stretch bond C-H(1429cm^{-1}). Peaks around 1428cm^{-1}are assigned to C-H aliphatic bending bond. The peak at 1244cm^{-1} is attributed to the bending bond of C-H adjacent to Cl. The C-C stretch bond of the PVC back bone chains corresponds to 1095cm^{-1} and the peaks at 745cm-^{1} correspond to C-Cl bond.

Figure 2 represents the spectra for PMMA, with stronger bands in region of 1143cm^{-1} corresponds to C-O stretching vibrations. The peak indicating presence of C=O stretching is 1721cm^{-1}, peak at 749 cm^{-1} correspond to C-H bending. The band at 1439cm^{-1} correspond to symmetric bending vibration of methyl group and the band or peak at 2924cm^{-1} correspond to C-H stretch.

Figure 3 represents the spectra for 75% PMMA/25%PVC blend, with the peak position for the C=O stretching appears at 1728cm^{-1} in PMMA shows slight shifting in the blend. New peak appeared as a result of addition of glycerol with a wave number of 3322cm^{-1} corresponds to O-H stretch and is broad. Peak position for C-O stretching reduces to 1039 cm^{-1} as a result of blending and also peak position for C-CI shows slight shifting from 750 cm^{-1} to 752 cm^{-1}.

Table 1: Liquid absorption behavior of the blends for different composition

			Day 1		Day 2		Day 3	
S/N	Composition (%)	Wi	Wf	% absorption	Wf	% absorption	Wf	% absorption
1	25/75	0.74	0.91	22.97	0.93	25.68	0.94	27.03
2	40/60	0.86	0.95	10.47	0.97	12.79	0.98	13.95
3	50/50	0.90	0.93	3.33	0.95	5.56	0.98	8.89
4	60/40	0.43	0.56	30.23	0.58	34.88	0.59	37.21
5	75/25	0.20	0.33	65.09	0.39	95.00	0.37	145.00
6	80/20	0.37	0.46	24.32	0.53	43.24	0.57	54.05

Wi = Initial weight of blend before immersion in water, W_f = Weight of blend after immersion in water.

The findings as shown in Table 1 above, compositions of 75/25 and 50/50 of PMMA/PVC were found to have highest (65.09, 95.00 and 145.00) and lowest (3.33, 5.56 and 8.89) liquid absorption respectively. The result pointed out as well, a positive correlation between increase in weight of each blend percentage liquid absorption from day 1 to day 3. This would be as a result of the presence of starch in the blends, which usually aid water absorption due to its hydrophilic nature (Abdelghany *et al.,* 2015). Starch polar nature owing to the presence of – OH group, in turn permit hydrogen bonding to formed in the water there by affecting the resistivity of the mixture (Abdelghany *et al.*, 2015).

Optical parameters of the blends

The optical constants/parameters are very important because they describe the optical behavior of a materials (Peesan *et al.,* 2007; (Hamad *et al.,* 2011).).The absorption and Extinction coefficient of the materials used in the study were determined based on the absorbance of the blends set at a particular wavelength (Subban and Arof, 2004; Hamad *et al.*, 2011; Kankel, 2014). The variation of absorption with wavelength of the incident light was recorded using UV/VISIBLE in the wavelength optical range of 1000-199.9 nm for polymer blend (Hamad *et al.,* 2011). Absorption of PMMA/PVC blend showed absorption changes in the wavelength range which depend on polymer type and the concentration of the polymer blend. The Absorption coefficient (a) and Extinction coefficient (k) have been recorded using the formula reported by Kankel (2014) and Abdelghany *et al.* (2015).

$$\alpha = \frac{(2.303\mathrm{A})}{tk} = (\mathrm{A}\lambda)4\pi \ldots\ 2$$

(Kenkel, 2014; Abdelghany *et al.*, 2015; Hamad *et al.*, 2011)

where,

α= Absorption coefficient and is defined as the ability of the blend to absorb light at a given wavelength.

A = is the absorption of the blend

k= Extinction coefficient in cm^{-1}

λ = Wavelength in nm

t= thickness of the blends in cm

Table 2: Optical parameters with variation in wavelength

S/N	Composition(w/w)	Wavelength(nm)	Absorbance	Thickness (cm)	Absorption coefficients (α)	Extinction coefficient (k)
1	75/25	904.9	0.479	0.1	11.03	34.49
		360.0	1.072	0.1	24.69	30.71
2	50/50	904.9	0.541	0.2	6,23	38.95
		275.0	4.042	0.1	3166.63	88.4
3	25/75	904.9	0.479	0.1	11.03	34.49
		295.0	3.988		91.84	93.61
4	60/40	904.9	0.249		5.73	17.93
		289.9	3.277	0.1	75.47	75.59
5	40/60	904.9	0.249	0.1	5.73	17.93
		289.9	3.277		75.47	75.59
6	80/20	904.9	0.243		5.60	17.50
		280.0	10.00	0.1	230.3	222.79

From the Table 2 both α and k shows a significant variation between samples, and all the blends absorb at 904.9 nm with constant thickness throughout except for 50 % PMMA + 50 % PVC composition with a value of 0.2 cm. The blend 25 % PMMA/75% PVC composition has the highest value of (k) and it was display toward the long wavelength of 295nm. Strong Absorption clear between 200 – 300nm respectively, 50% PMMA/50% PVC showed the best optical properties/parameters.

Degradation study

Soil burial experiment

It was observed that a remarkable degradation was indicated in the blends, which were in contact with soil microbes.

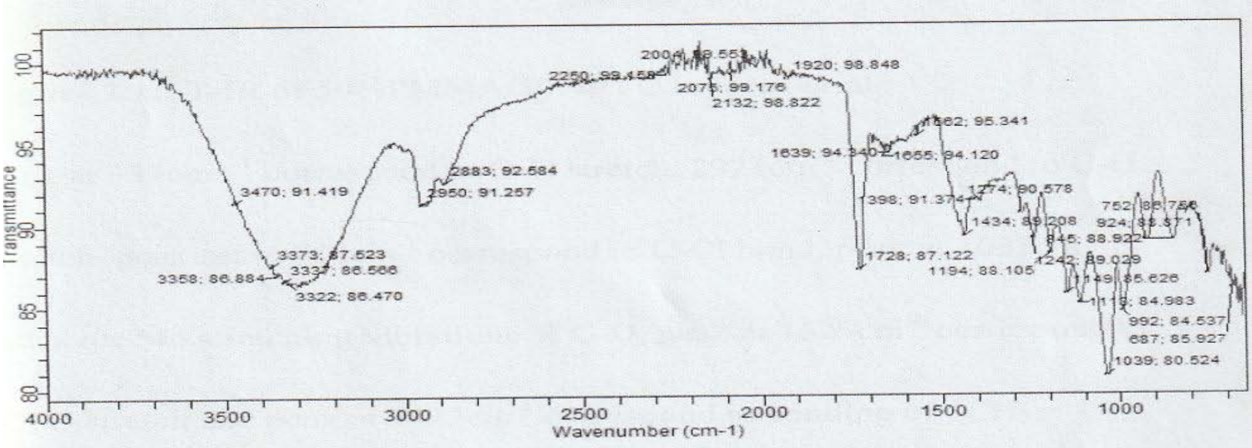


Figure 4: shows FT –IR spectrum of 75% PPMA 25% PVC before burial

Figure 4 illustrates C=O stretching at 1728cm^{-1}, peak at 3322cm^{-1} correspond to O-H stretch, Peak at 1039cm^{-1} correspond to C-O stretch, Peak position for C-CI bond is 752cm^{-1} and 1424cm^{-1} correspond to – CH_3 bending.

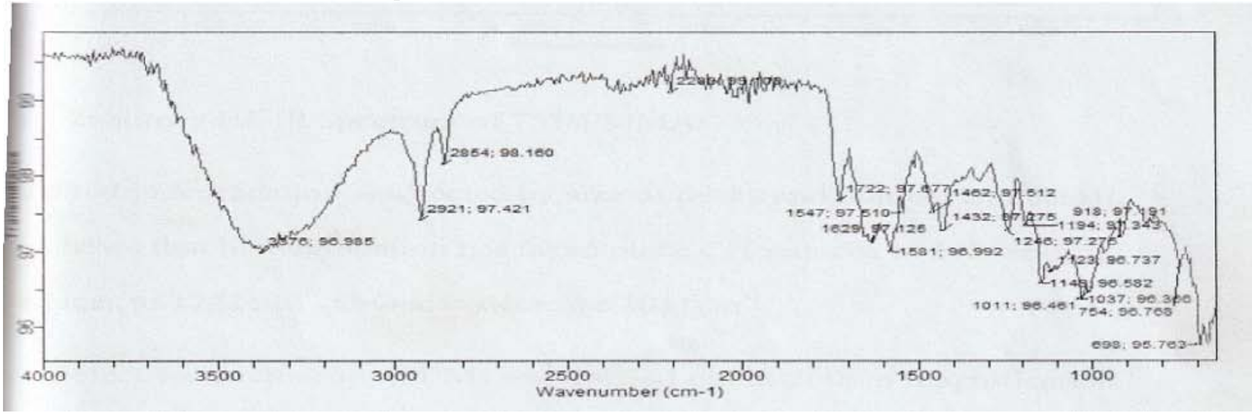


Figure 5: FT – IR of 50% PMMA/50% PVC before burial

Figure 5 indicated Peak at 3376 cm^{-1} correspond to O-H stretch, 2921cm^{-1} corresponds to C-H stretch, peak set at 754 cm^{-1} correspond to C-C1 bond, peak at 1037cm^{-1} is attributed to stretching vibrations of C-O, peak at 1627cm^{-1} correspond to C=O stretch and peak at 1432cm^{-1} correspond to binding of – CH_3.

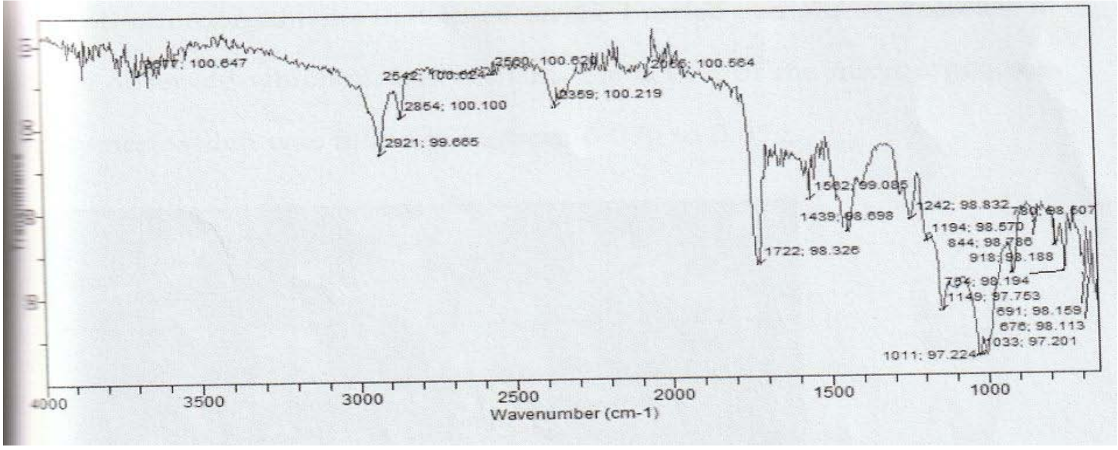


Figure 6: FT –IR spectrum of 75% PMMA 25% PVC after burial

Figure 6 showed that, IR related to biodegradation is affected by both size and number of peaks. If it reduces, it shows that biodegradation has taken place. CH reduces to 2921cm^{-1}, C=O reduces to 1722cm^{-1}, C-O also decrease 1011cm^{-1}.

Figure 7 shows the morphology of the sample before burial. The result shows the presence of whitish layers dispersed on the sample surface. However, after burial the whitish layers tend to disappear in some of the portions of the sample as seen in Figure 8. This was due to the action of soil microorganism that acted on the buried sample. A significant (28%) decrease in weight was observed which clearly confirm the action of the microorganisms on the polymer, from 0.07g to 0.05g.

Figure 7: SEM of 75% PMMA 25% PVC blend before burial

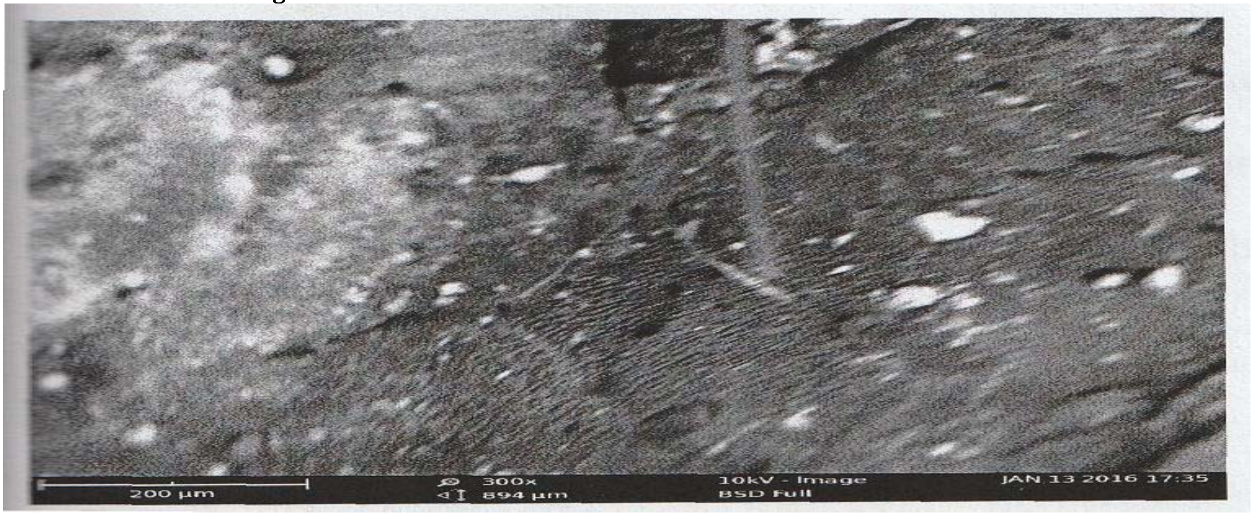


Figure 8: SEM of 75%PMMA/25%PVC blend after burial

CONCLUSION

It can be observed that, a PMMA/PVC blend was successfully prepared and characterized. This was confirmed by the differences observed in the FT – IR spectra of the PMMA/PVC blend and how it is differentiated from the spectra of the individual polymer components. The blend with the 75% PMMA and 25% PVC composition was found to have the best liquid absorption characteristics, with the following percentage absorption from day one to day three being 65.09%, 95.00% and 145%, respectively. Highest absorption coefficient (α) was observed in 50% PMMA 50% PVC blend at 3166.63 and the highest extinction (k) 222.79 was observed at 280.0nm.SEM demonstrates the homogeneity and miscibility of all ratios of prepared blends, and as well proved that, micrograms caused decrease in weight of the samples after burial experiment which confirmed the degradation by microbes on the blends. Optical absorption data from UV/Visible result shows a change in the optical energy gap assuming both direct and indirect transitions and ascertain that optical parameters of such blend was a compositional dependent. However, based on the outcome the research, there is a strong clue of likelihood of generating improve grade of polymers from studied polymer blends.

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