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Utilization of hazardous materials in oil based mud waste to turn into value added polymeric nanocomposite materials

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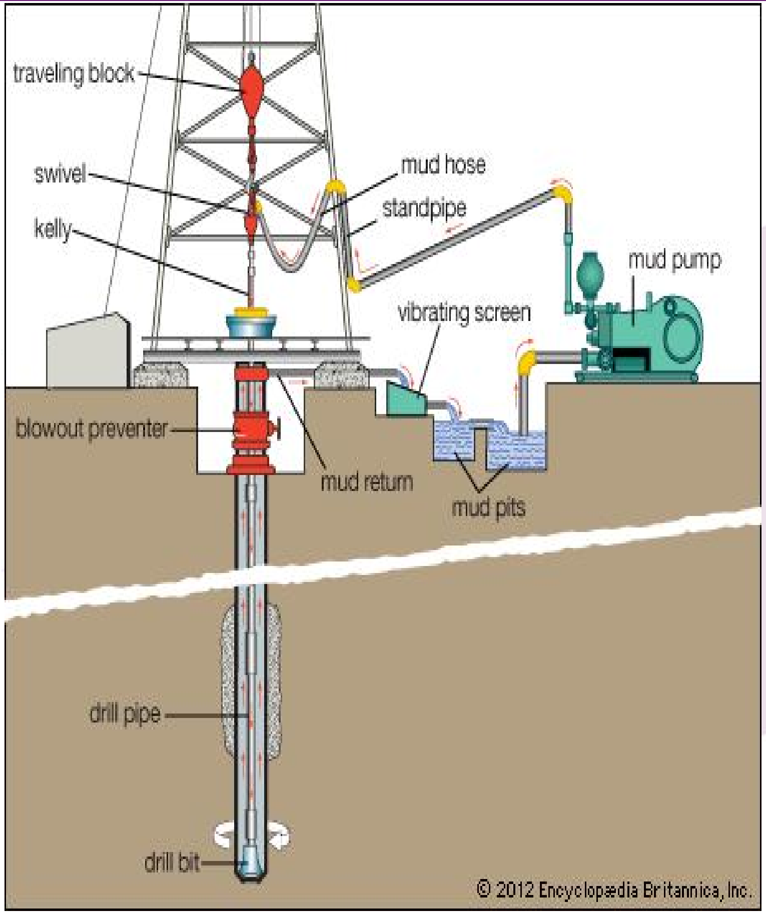
Outline

- Background
- Aim & objectives
- Methodology
- Analysis
- Results discussion
- Conclusion

Background



Existing oil based mud (OBM) waste treatment methods

- Physical treatment
- Chemical process
- Biological process
- Thermal treatment

Fig. 1: The circulation of drilling mud during the drilling of an oil well.
Source: https://www.britannica.com/technology/drilling-mud

Existing OBM waste management options (based on cost, time, efficiency)

Treatment	Time	Cost *(AUS$)	Advantages	Disadvantages
Composting	56-8 days	60-80	useful by-product	air emission, fire risk
Land farming	200-800 days	10-12	low cost	Environmental pollution
Land treatment	400-1200 days	4-5	low cost	long-term monitoring
Bio augmented landfarming	100-200 days	15-20	low cost	intense monitoring needed
Burial pit	500-3000 days	10-12	on site treatment	long term monitoring needed
Landfills	300-2500 days	40-60	relatively low cost	long term monitoring needed; legislative issues; slow biodegradaing rates
Bio reactors	10-30 days	700	rapid process	large cost; expertise needed; maintenance issues
Vermiculture	28-56 days	80-100	useful by-product	suitable for a limited range of pollutants
Chemical solidification/stabilisation	1-2 tonnes/h	100-250 (plus disposal costs)	rapid process	large set-up cost; risk associated with long term stabilisation
Incineration	5-6 tonnes/h	500-1000	waste reduction	large set-up and running cost; may not remove all pollutants
Thermal desorption	3-10 tonnes/h	400-1500	waste reduction and low retention time	large set-up and running cost;

Source: Ball AS, Stewart RJ, Schliephake K. A review of the current options for the treatment and safe disposal of drill cuttings. *Waste Manag Res* 2012 May;**30(5)**:457-473.

Thermomechanical Cuttings Cleaner (TCC)

Sustainable solution

???

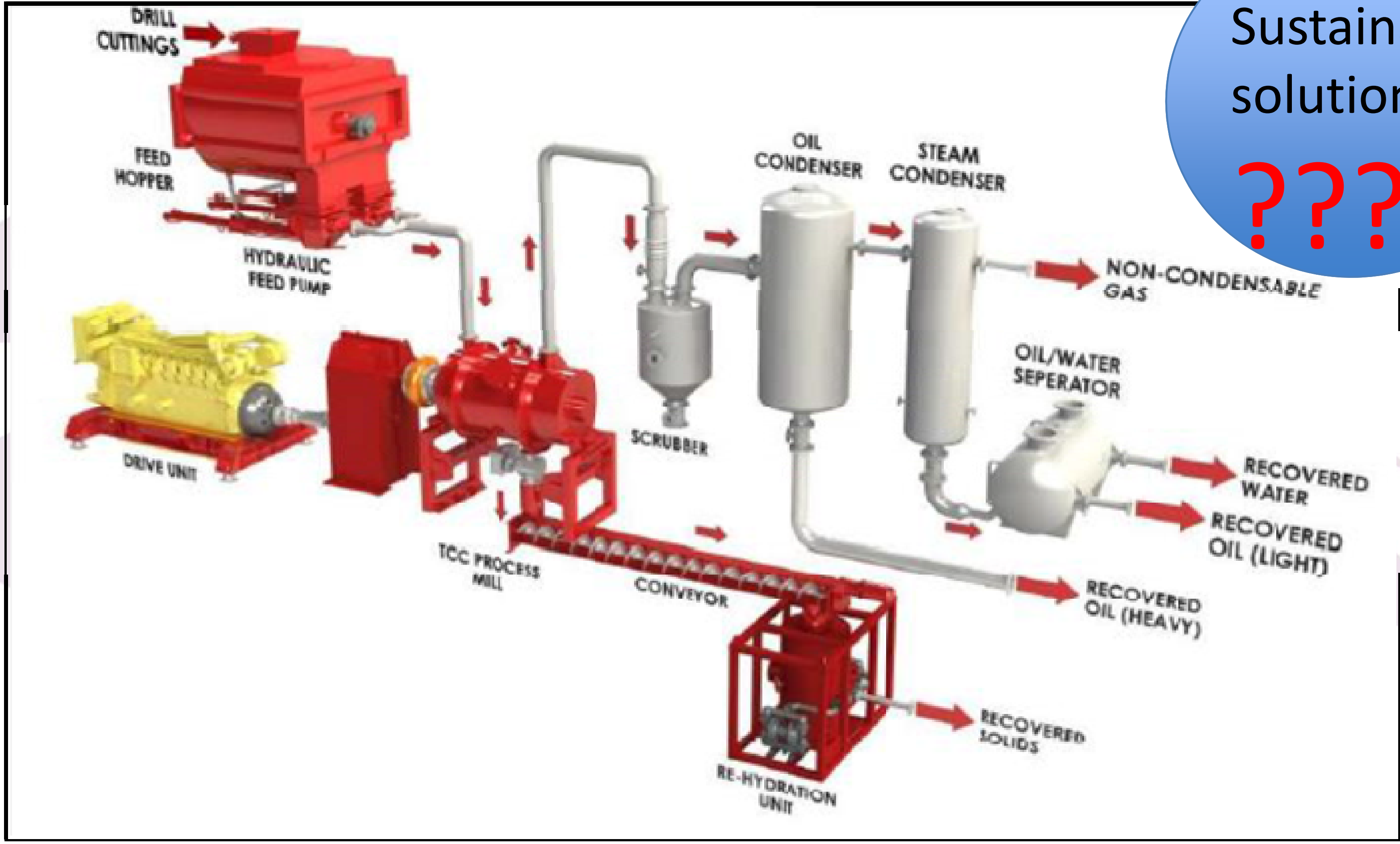
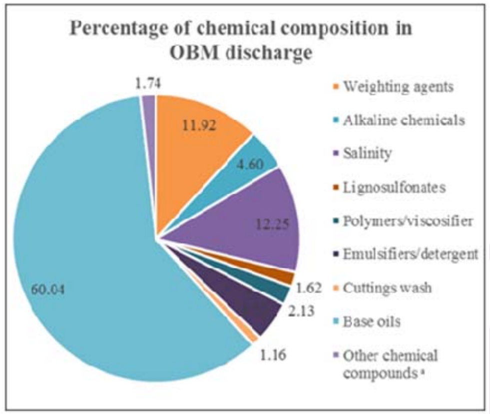
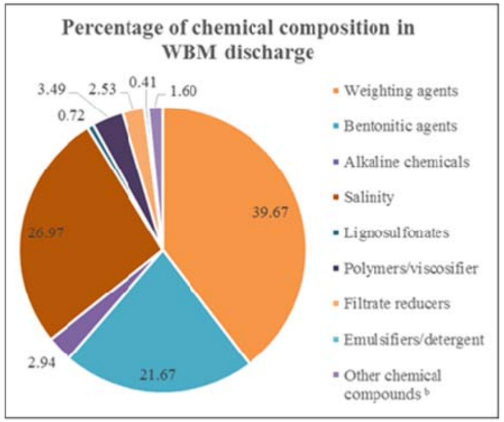


Fig. 2: Diagram of TCC system

Source: http://www.halliburton.com/en-US/ps/baroid/fluid-services/waste-management-solutions/waste-treatment-and-disposal/thermal-processing-systems/thermomechanical-cuttings-cleaner-tcc.page

OBM waste composition as a hazardous material





List I and II pollutants in environment

Type of pollutants	Members of pollutant groups
	Organohalogen compounds and substances
	Organophosphorus compounds
	Organotin compounds
List I	Carcinogenic substances
	Mercury and its compounds*
	Cadmium and its compounds*
	Persistent mineral oils and hydrocarbons of petroleum origin
	Persistent synthetic substances
	Certain metals, metalloids, and their compounds: 1) Zinc 2) Copper* 3) Nickel* 4) Chromium (Cr(VI)*) 5) Lead* 6) Selenium* 7) Arsenic* 8) Antimony* 9) Molybdenum 10) Titanium 11) Tin* 12) Barium 13) Beryllium 14) Boron 15) Uranium 16) Vanadium 17) Cobalt 18) Thalium* 19) Tellurium* 20) Silver
	Biocides and their derivatives
List II	Toxic or persistent organic compounds of silicon and its substances
	Inorganic compounds of phosphorus and elemental phosphorus
	Non persistent mineral oils and hydrocarbons of petroleum origin
	Cyanides and fluorides
	Substances causing oxygen imbalance such as ammonia, nitrites

*: Hazardous waste classified in according to Directive 2008/98/EC

Fig. 3: Percentage of individual chemical constituents present in OBM and WBM discharge adapted from Hudgins .

Source: Siddique S, Kwoffie L, Addae-Afoakwa K, Yates K, Njuguna J. Oil Based Drilling Fluid Waste: An Overview on Environmentally Persistent Pollutants. In IOP Conference Series: Materials Science and Engineering 2017 May (Vol. 195, No. 1, p. 012008). IOP Publishing.

Aim and Objectives

Aim:

To understand and evaluate the crystallinity and thermal degradation behaviour of PA6 nanocomposites using reclaimed clay from oil based drilling fluids waste.

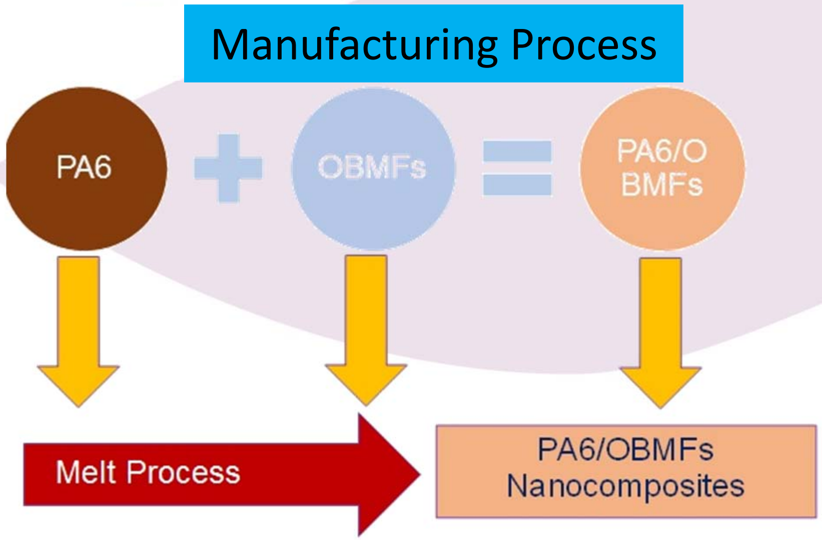
Objectives

1. Morphology investigation of PA6/OBMFs nanocomposites using SEM.
2. Elemental analysis of PA6/OBMFs nanocomposites using EDXA.
3. Chemical structure analysis using FTIR technique.
4. PA6/OBMFs nancomposites decomposition study using TGA.
5. Degradation study of PA6/OBMFs nancomposites using DSC.

Methodology

Materials and experiments

- Matrix material
  - PA6
- Nanofiller
  - OBMFs (Thermally treated)



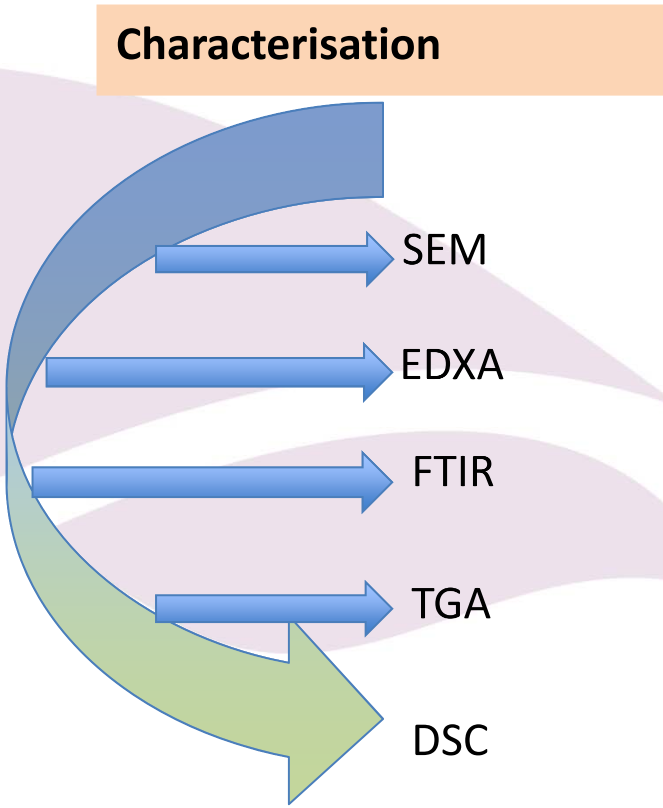


Fig. 4: Schematic representation of (a) PA6/ OBMFs nanocomposite manufacturing process and (b) different experimental analysis of PA6/ OBMFs nanocomposite.

SEM analysis

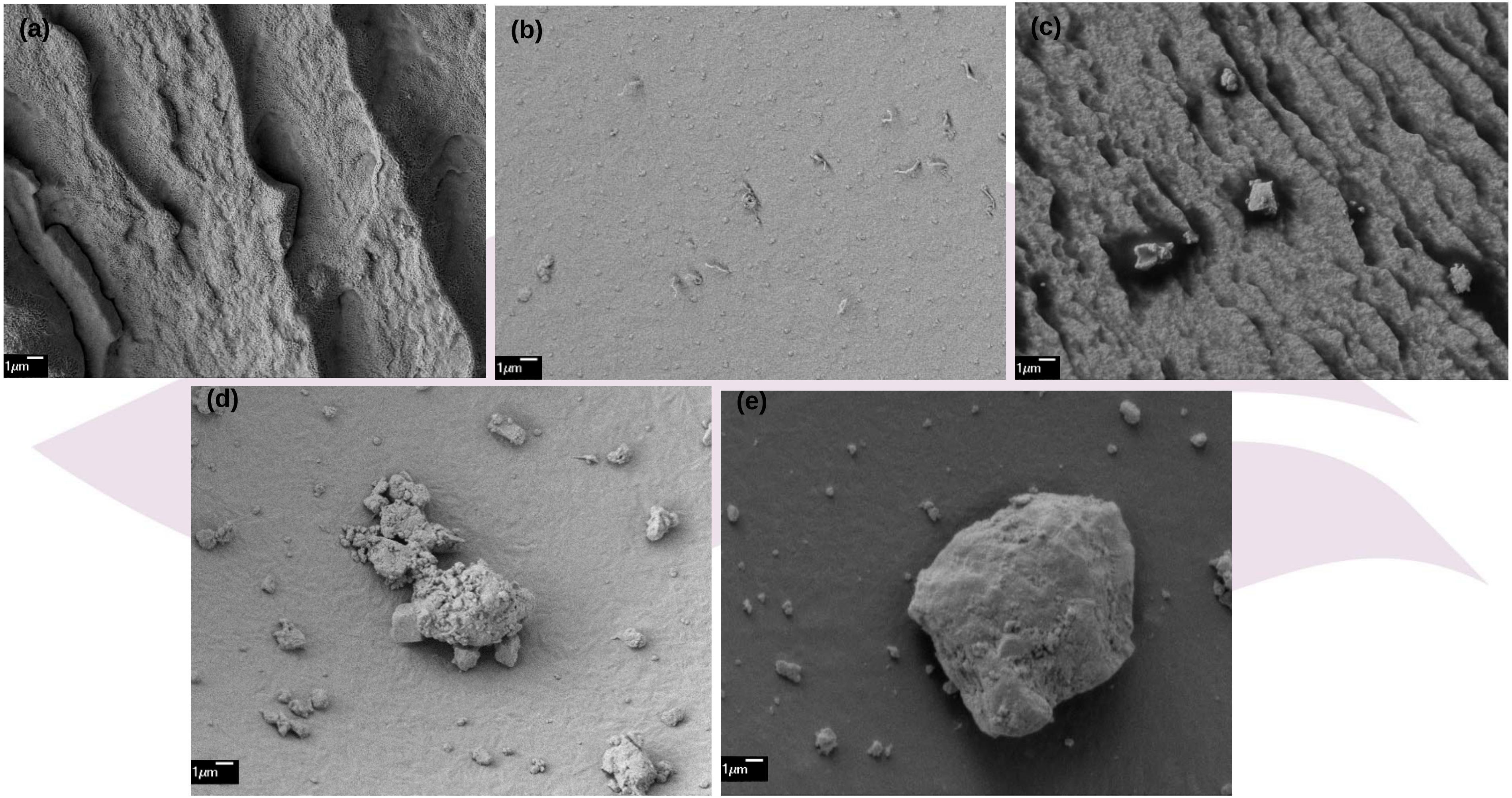


Fig. 5: SEM images of (a) PA6; (b) PA6 with 2.5 wt% OBMFs; (c) PA6 with 5.0 wt% OBMFs; (d) PA6 with 7.5 wt% OBMFs; and (e) PA6 with 10.0 wt% OBMFs.

EDXA analysis

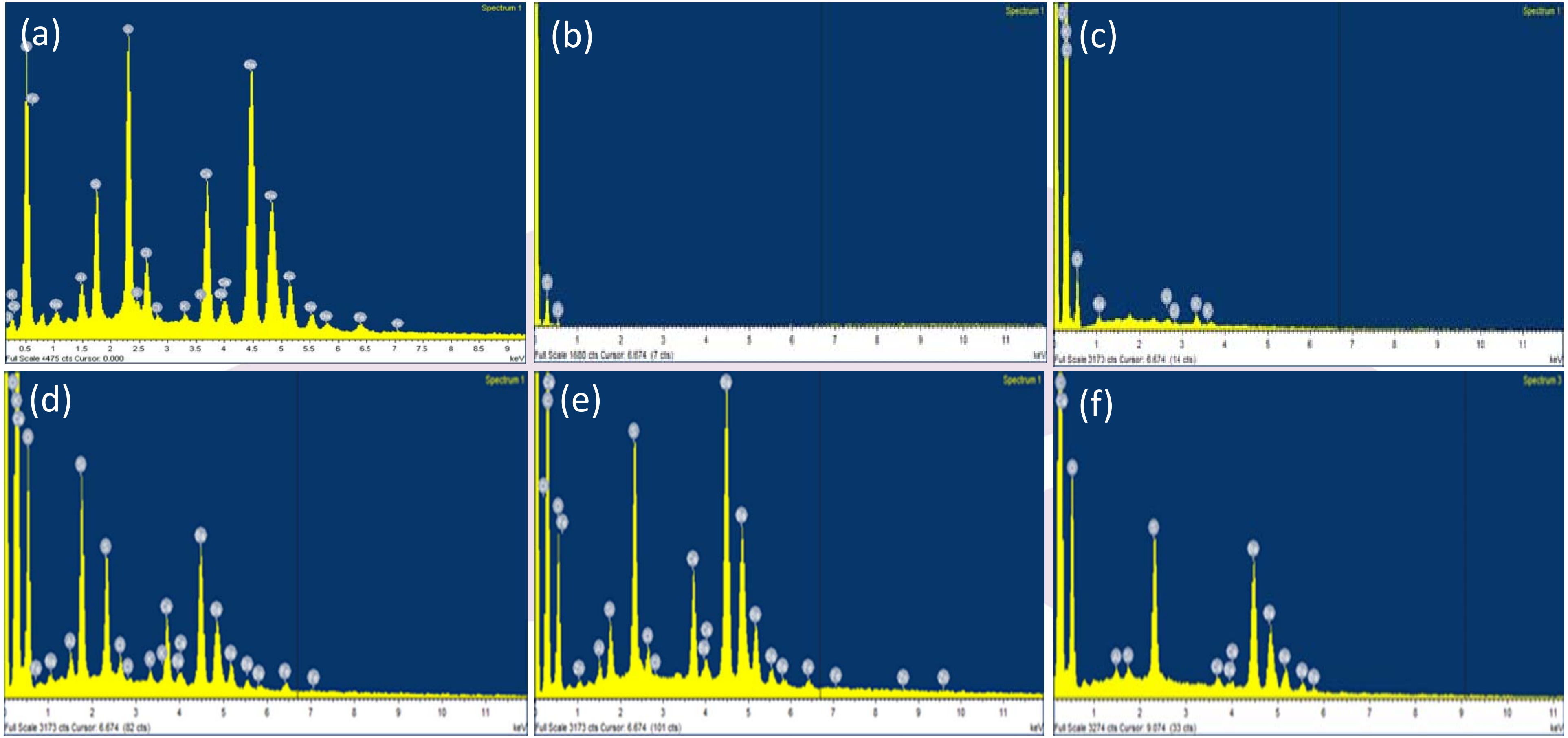


Fig. 6: EDX spectra of (a) OBMFs; (b) PA6; (c) PA6+2.5 wt% OBMFs; (d) PA6+5.0 wt% OBMFs; (e) PA6+7.5 wt% OBMFs and (f) PA6+10.0 wt% OBMFs.

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FTIR analysis:

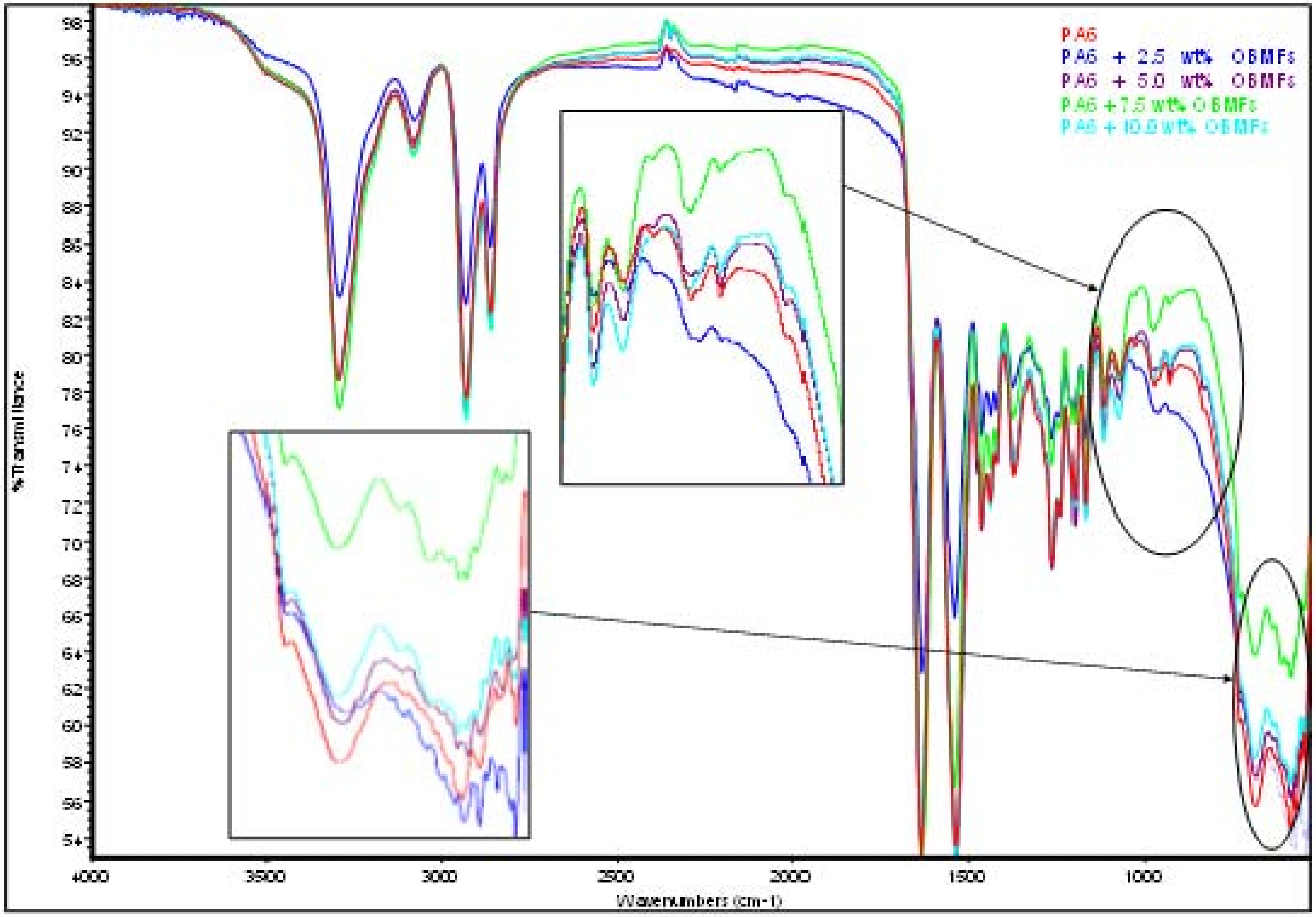

Fig. 7: Comparison of FTIR full scale spectra of PA6 and its nanocomposite.

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ATR FT-IR peak assignments

Wave number (cm^{-1})	Assignments
3295	Hydrogen-bonded N-H stretching
3079	Fermi-resonance of N-H stretching
2930	$V_{as}(CH_{2})$
2859	V_s(CH2)
1633	Amide I
1539	Amide II
1462	CH_2 deformation
1435	CH_2 deformation
1370	Amide III & CH_2 wag
1259	Amide III & CH_2 wag
1200	Amide III & CH_2 wag
1169	CO-NH, skeletal motion (Am)
1118	C-C stretching (Am)
1074	C-C stretch (Am)
973	CO-NH in plane vibration
680	Amide V
525-580	Primary aliphatic nitriles (CΞN)

Decomposition behaviour of PA6 and its nanocomposite

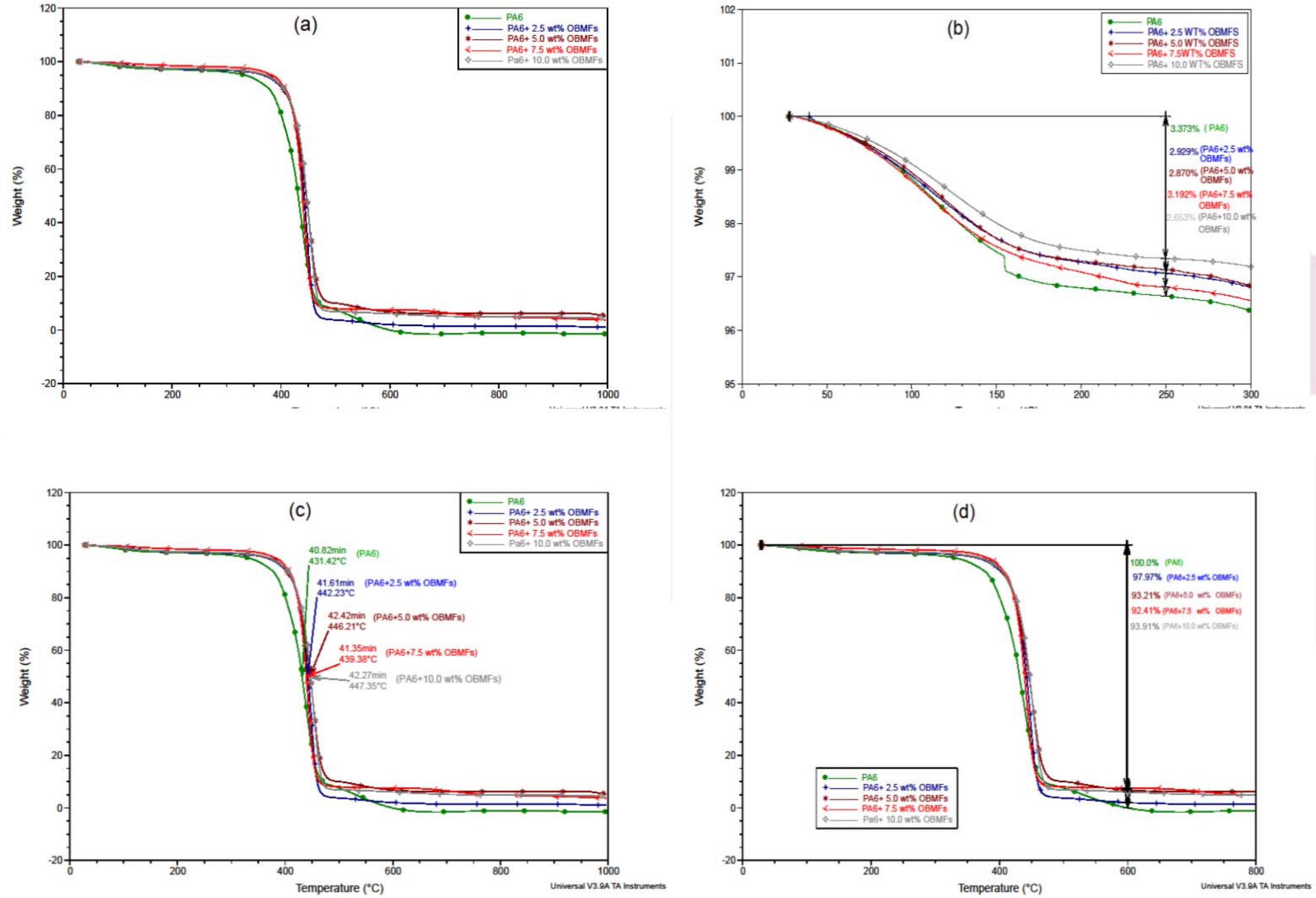

Fig. 8: TGA of PA6 and PA6/OBMFs nanocomposites at: (a) complete thermograms of all samples; (b) 250°C; (c) D ½; (d) 600 °c.

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TGA analysis at different decomposition stages of PA6 and its nanocomposites

Material	% wt loss at 250 °C	$T_{D10\%}$ (° c)	$T_{D50\%}$ (° c)	D 1/2 Time	Residue (% wt) at 600 °C
PA6	3.37	399.24	431.42	40.82	0.00
PA6+2.5 wt% OBMFs	2.93	407.77	442.23	41.61	2.03
PA6+5.0 wt% OBMFs	2.87	416.87	446.21	**42.42**	6.79
PA6+7.5 wt% OBMFs	3.19	412.32	439.38	41.35	7.59
PA6+10.0 wt% OBMFs	2.65	**416.87**	**447.35**	42.27	6.09

Degradation behaviour of PA6 and its nanocomposite

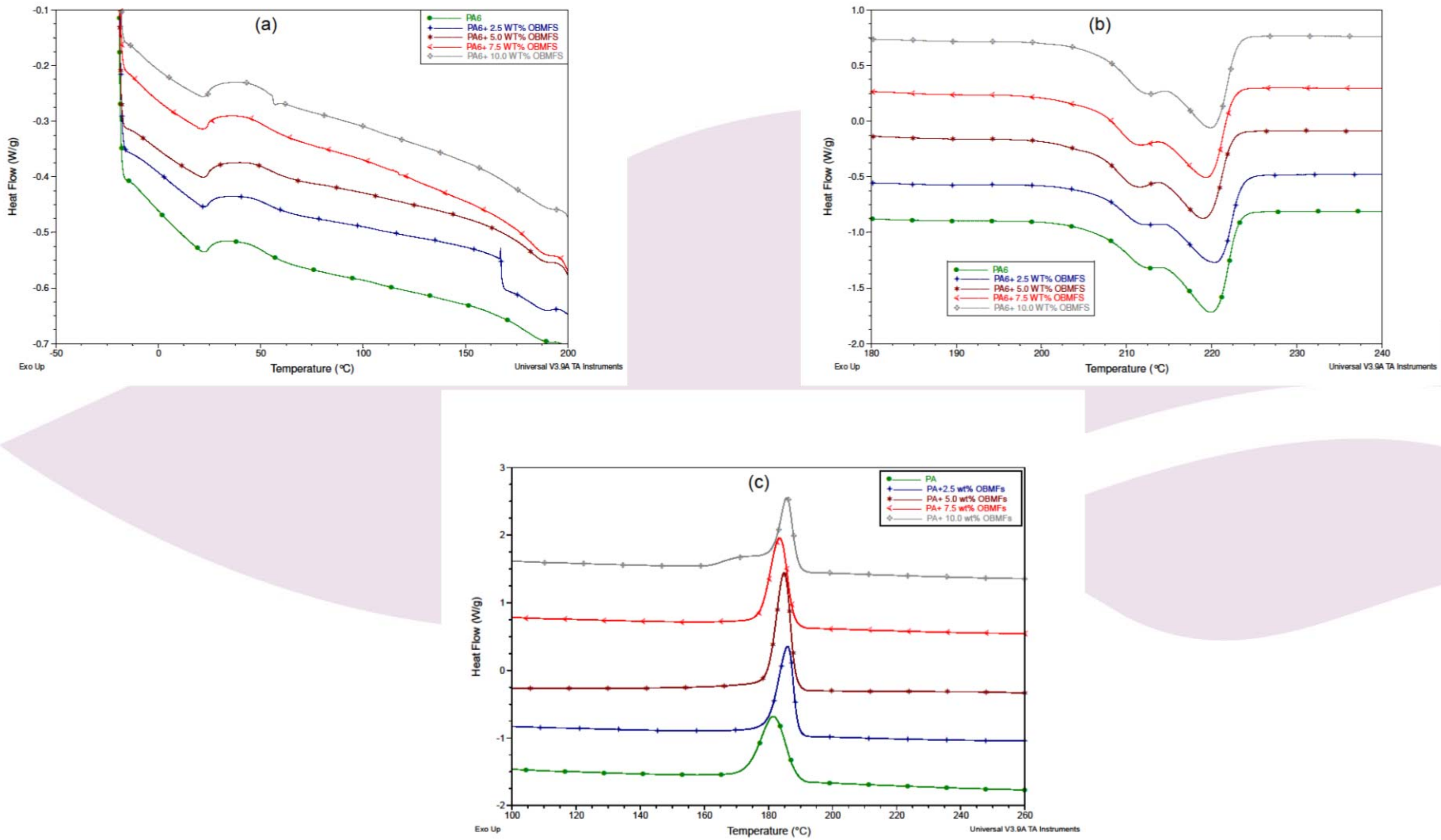

Fig. 9: DSC thermograms of PA6 and its nanocomposites at (a) Tg; (b) T_m and (c) T_c.

% of crystallinity calculation

% crystallinity= [ΔHm - ΔHc]/ΔHm^0 * 100%

Material	ΔHm (J/g)	ΔHc(J/g)	ΔHm-ΔHc(J/g)	((ΔHm-ΔHc)/ΔHm°) *100%
PA6	52.83	0	52.83	22.96
PA6+2.5 wt% OBMFs	48.05	0	48.05	20.88
PA6+5.0 wt% OBMFs	49.32	0	49.32	21.43
PA6+7.5 wt% OBMFs	51.56	0	51.56	22.41
PA6+10.0 wt% OBMFs	50.73	0	50.73	22.05

Heat Capacity Calculation

$$C_p = (\delta Q/\delta t) \times (\delta t/\delta T)$$

Material	Mass of samples (m) mg	Heat capacity (J/g)	Specific heat capacity (Cp) $Jk^{-1}kg^{-1}$
PA6	6.20	60.57	2523
PA6+2.5 wt% OBMFs	6.30	55.87	2327
PA6+5.0 wt% OBMFs	6.30	57.66	2402
PA6+7.5 wt% OBMFs	7.80	60.55	**2522**
PA6+10.0 wt% OBMFs	6.30	64.69	**1321**

Schematic diagram of RAF and MAF

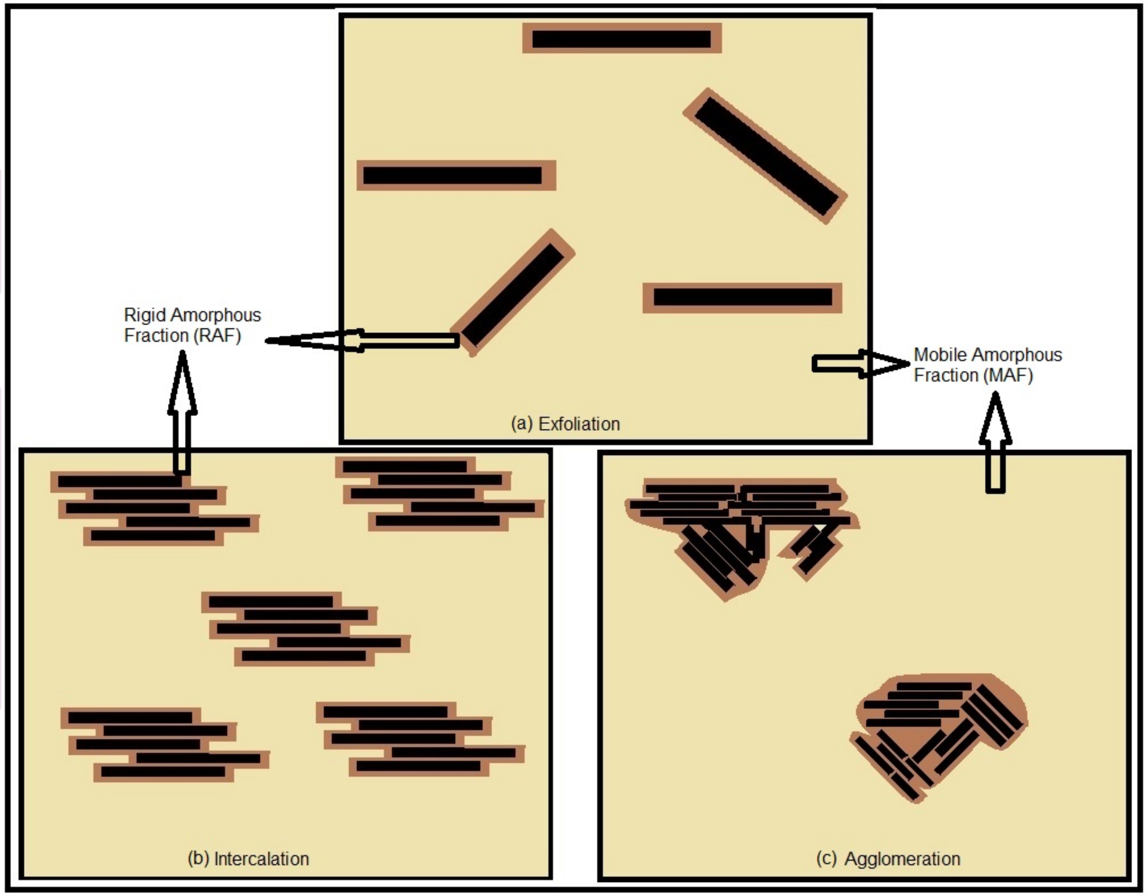

Fig. 10: Schematic diagram of OBMFs platelets associated with MAF and RIF of PA6 matrix

RAF and MAF Calculation

MAF= (ΔCp/ΔCp(am)) *100%

RAF= 1- crystallinity - $\Delta C_p/\Delta C_{p\ pure}$ **or** ***RAF'= 1- filler content- $\Delta C_p/\Delta C_{p\ pure}$***

Material	MAF	CF	CF'	RAF= 100-MAF-CF	RAF'= 100-MAF-CF'	**TIF**
PA6	27.26	22.96	0.00	49.78	72.74	**72.74**
PA6+2.5 wt% OBMFs	27.46	20.88	2.50	51.66	70.04	**72.54**
PA6+5.0 wt% OBMFs	58.91	21.43	5.00	19.66	36.09	**41.09**
PA6+7.5 wt% OBMFs	46.01	22.41	7.50	31.58	46.49	**53.99**
PA6+10.0 wt% OBMFs	55.04	22.05	10.00	22.91	34.96	**44.96**

Relation between TIF and filler dispersion

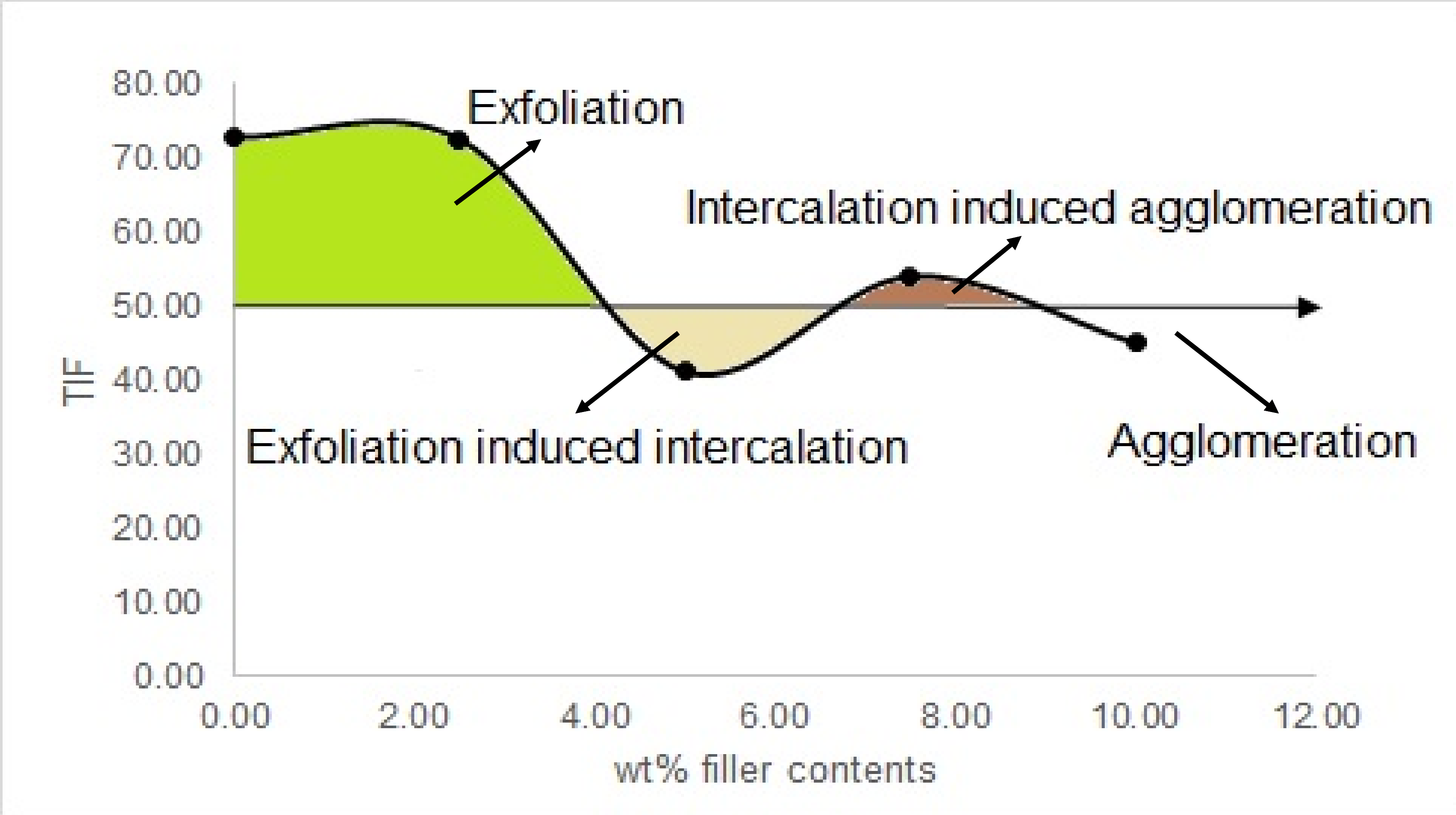

Fig. 11: Relation between TIF and dispersion behaviour of OBMFs in PA6 matrix

Conclusion

- In TGA, the % weight loss of PA6/OBMFs nanocomposites decreases with the incremental weight % of OBMFs in PA6/OBMFS nanocomposites
- There is not any significant heat capacity property changes for PA6 with 2.5 wt%, 5.0 wt% and 7.5 wt% OBMFs nanocomposites
- There is a drastically heat capacity (about 47%) reduction noticeable for PA6 with 10.0 wt% nanocomposite
- 50% TIF line deduce the degree of dispersity in PA6/OBMFs nanocomposites

Thank You