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**"Effect of Sepiolites/Organo Sepiolites Fillers on Mechanical Morphological and Thermal Characteristic of Dioctylphthalate-Plastised Polyvinyl Chlorides"**

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# Effect of Sepiolites/Organo-Sepiolites Fillers on Mechanical, Morphology and Thermal Characteristics of Maleic Anhydride/Buthyl Acrylate-Modified and Diocthyphthalate-Plastisised Polyvinyl Chlorides

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**Abstract.** Polyvinylchloride (PVC) resins, have been used widely as versatile engineering materials, and various reseachers have reported research works to improve technical specifications and to widen utilisations of the PVC resins. Furthermore, for utilisations as flexible engineering thermoplastics, the PVC resins have been plastisised for example using diocthyphthalate (DOP). However, the plastisised thermoplastics were more susceptible to heat and fire environments, and to overcome the problems, during their manufactures the plastisised PVC (pPVC) resins have been incorporated with various commercial heat stabilisers and fire retardants, such as zincstearate (ZS) and ammonium polyphosphates (APP). Sepiolites, as one type of pillared-clays and having chemical structure as hydrated magnesium silicates, have been used as fillers for rubber blends, which functioned not only as reinforcements but also as thermal stabilisers. It has been further reported that thermal stabilizing actions of sepiolites in rubber blends were due to their ability to form char during combustions which covered surfaces and inhibit diffusion of oxygen into the rubber blends. To improve compatibility in hydrophobic rubbers/thermoplastics blends, prior to their utilisations sepiolites have been modified with various organic surfactants, such as cetyl trimethylammonium bromide (CTAB). Moreover, various comonomers, such as maleic anhydride (MA) and buthyl acrylate (BA), have been incorporated/grafted into the rubbers/thermoplastics blends. When compared to commercial thermal stabilisers and flame retardants, thermal stabilizing activity of sepiolites were more substantive and able to stay longer and nondegradable in the rubber/thermoplastics blends. Here, the effects of sepiolites/organo (CTAB)-sepiolites on mechanical, morphology, and thermal properties of diocthyphthalate (DOP)-plastisised and maleic anhydride/buthyl acrylate (MA/BA)-modified PVC blends have been studied. It was found that the main possible reactions in the modification procedures were grafting and crosslinking of MA and BA comonomers or comonomer homopolymers onto the PVC resins. When compared to those of their corresponding original sepiolites, the organo-sepiolites promoted higher tensile strengths and elongation at breaks, due to better compatibility of the later in the pPVC-g-MA/BA blends. Modification with MA and BA comonomers increased compatibility of sepiolites/organo-sepiolites-filled, and therefore improved morphology properties of pPVC-

g-MA/BA-Sep/Osep blends. The hydrous magnesium silicate sepiolites/organo-sepiolites fillers functioned as thermal stabilisers for pPVC-g-MA/BA blends, by formation of char residues which covered surfaces and inhibited oxygen diffusion into the decomposing pPVC blends, although the organo-sepiolites fillers possessed lower thermal stabilizer properties than those of their origin sepiolites fillers.

*Keywords:* Alphabetically sorted; Capitalized first word; From a to z; Maximum 5 keywords; Sentence case; Separate by semicolon (;) between keyword

## 1. Introduction

Polyvinylchloride (PVC) resins, have been used widely as versatile engineering thermoplastics. (Darvishi et al., 2015) Various researchers have reported research works to improve technical specifications and to enlarge utilisations of the PVC resins (Li et al., 2015). Hammiche et al., 2020 have prepared natural fibre-filled maleic anhydride (MA)-modified PVC composites and reported improved adhesion of the MA-modified PVC matrices on to the natural fibre filler surfaces, and hence increased their mechanical properties. Mahendra et al., 2019 have also used maleic anhydride-modified cyclic natural rubbers as adhesion promoters for cyclic natural rubber-polypropylene blends. (Salazar et al., 2017 have also modified PVC resins with maleic anhydride comonomer which then functioned as compatibilisers in PVC composites containing egg shell powder as fillers. It was reported that the newly prepared PVC composites possessed not only improved mechanical properties but also improved wettability and compatibility with hydrophilic surfaces. To improve their impact properties, Long et al., 2019 has blended PVC resins with buthyl acrylate (BA)/methyl methacrylate (MMA)-modified polystyrene (PS). The BA/MMA-modified PS has functioned as compatibiliser and lubricant for preparation of fresh PVC/PS blends. Furthermore, for utilisations as flexible engineering thermoplastics, the PVC resins have been plastisised for example using dioctylphthalate (DOP). However, the plastisised thermoplastics were more susceptible to heat and fire environments due to the presence of more thermal unstable and combustible plastisiers, Hirschler (2017). And to overcome the problems, the plastisised PVC (pPVC) resins have been incorporated with various commercial heat stabilisers and fire retardants, such as zincstearate (ZS) and ammonium polyphosphates (APP), during their manufactures. (Li et al., 2019)

Sepiolites, as one type of pillared-clays and having chemical structure as hydrated magnesium silicate:  $Si_{12}O_{30}Mg_8(OH)_4(OH_2)_4 \cdot (H_2O)_8$ , formed fibres 0.2-2  $\mu m$  long, and 5-30 nm in diameter, have been used as fillers for rubber blends, which functioned not only as reinforcements but also as thermal stabilisers. (Zaini et al., and Tang et al., 2017) have further reported that thermal stabilizing actions of sepiolites in rubber blends were due to their ability to form char during combustions which covered surfaces and inhibit diffusion of oxygen into the rubber blends. When compared to commercial thermal stabilisers and flame retardants, thermal stabilizing activity of sepiolites were more substantive and able to stay longer and nondegradable in the rubber blends. Zembouai et al., 2018 have studied synergistic actions of sepiolites and montmorillonite in poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/polylactic acid (PHBV/PLA) blends. It is well known that as clays fillers, sepiolites possessed low compatibility with hydrophobic polymer matrices, and therefore, prior to their utilisations they have been modified with various organic surfactants, such as cetyl trimethylammonium bromide (CTAB). To

improve compatibility with hydrophilic sepiolites fillers, especially in hydrophobic thermoplastics, various comonomers, such as maleic anhydride (MA and buthyl acrylate (BA), have been incorporated/grafted into the thermoplastics resins. Zaini et al., 2019 have utilized glutamine palmitate-modified sepiolites as coupling agent between sepiolites and EPDM matrix which improved dispersion and interface adhesion of the sepiolites fillers and increased tensile strength and elongation at breaks of the EPDM blends. So far, there has not been any works on the effects of sepiolites/organo (CTAB)-sepiolites on mechanical, morphology, and thermal properties of dioctylphthalate (DOP)-plastisised and maleic anhydride/buthyl acrylate (MA/BA)-modified PVCblends.

## 2. Methods

### 2.1. Materials

Polyvinylchloride (PVC) resin, sepiolites, cetyltriethylammonium bromide (CTAB), dioctylphthalate (DOP), maleic anhydride (MA), buthyl acrylate (BA), benzoylperoxide (BPO), tetrahydrofurane (THF), ethanol (absolute) and dichloromethane (DCM) were all ex. Sigma-Aldrich Chemicals and were used directly without any pretreatments.

### 2.2. Preparations of maleic anhydride/buthyl acrylate-modified PVC

Fresh PVC resin, maleic anhydride/buthyl acrylate (MA/BA), were mixed in tetrahydrofuran (THF) solvent under reflux and intensive stirring for 30 minutes, in the presence of benzoylperoxide (BPO) as initiator based on compositions as shown in Table 1. The mixtures were then casted on a glass plates, dried in open air and under vacuum at constant temperature 40°C to constant weight. The dried maleic anhydride/buthyl acrylate-grafted-PVC (MA/BA-g-PVC) blends were then cut to tensile test specimens according to ASTM D412-92 standard, (Wirjosentono et.al, 2019).

**Table 1** Constituents for preparations of MA/BA-g-PVC blends (phr: per hundred resin)

Samples	Constituent contents (phr)		
	Benzoylperoxide (BPO)	Maleic anhydride (MA)	Buthyl acrylate (BA)
PVC Control	0.4	-	-
PVC-g-MA5	0.4	5	-
PVC-g-MA10	0.4	10	-
PVC-g-MA20	0.4	20	-
PVC-g-BA5	0.4	-	5
PVC-g-BA10	0.4	-	10
PVC-g-BA20	0.4	-	20

### 2.3. Preparations of maleic anhydride/buthyl acrylate-modified PVC containing sepiolites/organo-sepiolites

Prior to utilizations, cetyltrimethylammonium bromide (CTAB: organo)-modified sepiolites were prepared by immersion of fresh sepiolites in saturated ethanol solution of

CTAB for 24 hours and then dried under vacuum at 40°C to constant weight, Acosta et.al (1986). Fresh PVC resin, sepiolites (Seps), (CTAB)-modified sepiolites (Oseps), were mixed in tetrahydrofuran (THF) solvent under reflux and intensive stirring for 30 minutes, based on compositions as shown in Table 2. The mixtures were then casted on a glass plates, dried in open air and under vacuum at constant temperature 40°C to constant weight. The dried maleic anhydride/buthyl acrylate-grafted sepiolites/organo-sepiolites-filled PVC (MA/BA-g-PVC-Seps/Oseps) blends were then cut to tensile test specimens according to ASTM D412-92 standard.

**Table 2** Preparations of MA/BA-g-PVC-Seps/Oseps blends (phr: per hundred resin)

Samples	Contents of components (phr)				
	Dioctylphthalate (DOP)	Maleic anhydride (MA)	Buthyl acrylate (BA)	Sepiolites	Organo-sepiolites
pPVC-g-MA/BA (Control)	30	10	10	-	-
pPVC-g-MA-Sep5	30	10	-	5	-
pPVC-g-MA-Sep10	30	10	-	10	-
pPVC-g-MA-Sep20	30	10	-	20	-
pPVC-g-MA-Osep5	30	10	-	-	5
pPVC-g-MA-Osep10	30	10	-	-	10
pPVC-g-MA-Osep20	30	10	-	-	20
pPVC-g-BA-Sep5	30	-	10	5	-
pPVC-g-BA-Sep10	30	-	10	10	-
pPVC-g-BA-Sep20	30	-	10	20	-
pPVC-g-BA-Osep5	30	-	10	-	5
pPVC-g-BA-Osep10	30	-	10	-	10
pPVC-g-BA-Osep20	30	-	10	-	20

#### 2.4 Characterisations of PVC blends

Dumbbell-shaped specimens were cut from the casted sheets and tested for their tensile strengths and elongation at breaks, according to ASTM D412-92, using a universal testing machine (Instron 3366) at a crosshead speed of 500 mm/min with 10 kN load. Morphology of surface fractures of the PVC blends were tested using scanning electron microscopy (VPFESEM), model Zeiss Supra 35-VP, Carl Zeiss NTS GmbH, Oberkochen, Germany after coating with a thin layer of gold-palladium. (Nasution et al., 2020) DSC analysis of the PVC blends were characterized using a

differential scanning calorimeter (DSC) METTLER TOLEDO, first and second heating procedures (heating range 30°-200°C, heating rate: 10°C/minute). TGA analysis of the PVC blends were characterized using Shimadzu DTG-60 thermogravimeter, (heating range 30° – 600°C, heating rate: 10°C/minute) (Saragih et al., 2020)

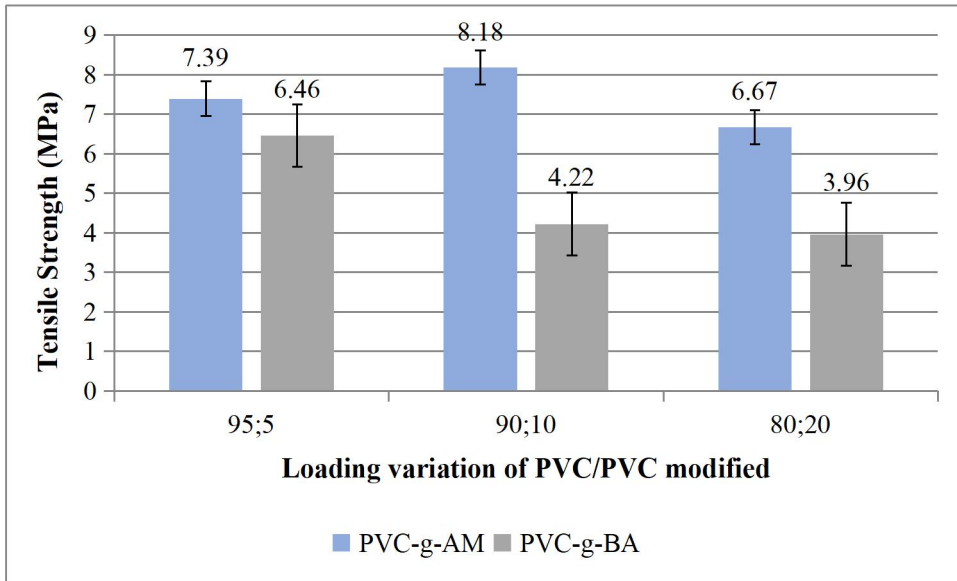
### **3. Results and Discussion**

#### *3.1 Modification of polyvinylchloride (PVC) with maleic anhydride and buthyl acrylate comonomers*

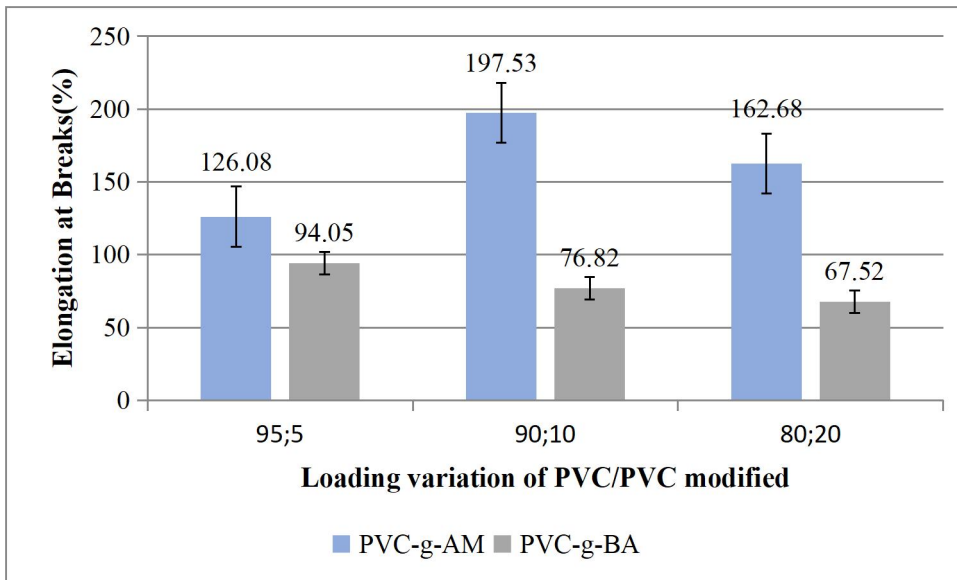
Modification reactions of PVC with maleic anhydride (MA) and buthyl acrylate (BA) comonomers were carried out under reflux in THF solution in the presence of benzoylperoxide (BPO) initiator as in Procedure 2.2, using formula in Table 1. Efficiency of the modification reactions were analysed using mechanical tests, electron microscopy, thermal analysis (DSC and TGA), and FTIR spectroscopy, as in procedure 2.4.

##### 3.1.1 Mechanical properties

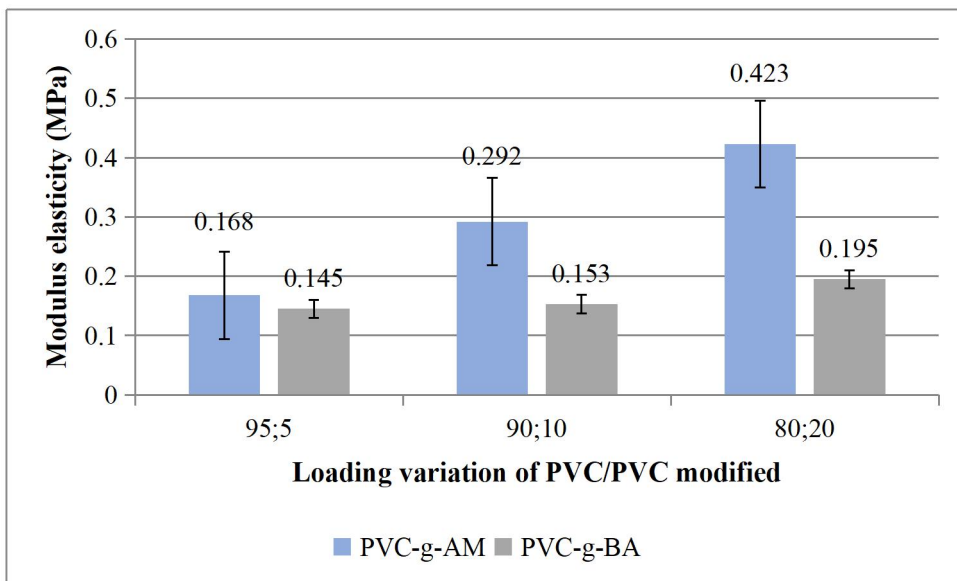
Figures 1 and 2 showed tensile strengths and elongation at breaks of PVC-g-MA blends compared to those of PVC-g-BA at various loading of the comonomers. In the case of PVC-g-MA blends increased of MA loading to 10 phr increased tensile strength (7.39-8.18 MPa) and elongation at breaks (126.08-197.53 %), but decreased again when the MA loading were increased to 20 phr, tensile strength (8.18-6.67 MPa) and elongation at breaks (197.53-162.68 %), In the case of PVC-g-BA blends, however, the tensile strengths and elongation at breaks were decreased stadily when tha BA loading were incised to 20 phr, tensile strength (6.16-3.96 MPa) and elongation at breaks (94.08-67.52 %). These evidences indicated that the MA comonomers were able to promote grafting and crosslinking reactions and the MA homopolymers were more compatible in the PVC blends than the BA comonomers in their corresponding conditions, Turhan et.al (2013). These were also supported by their modulus elasticity results shown in Figure 3, in which in the case of PVC-g-MA blends their modulus elasticity imcreased substantially (0.168-0.423 MPa), compared to those of PVC-g-BA blends, which almost unchanged when loadings of the comonomers increased to 20 phr.



**Figure 1** Tensile strengths of PVC-g-MA and PVC-g-BA blends



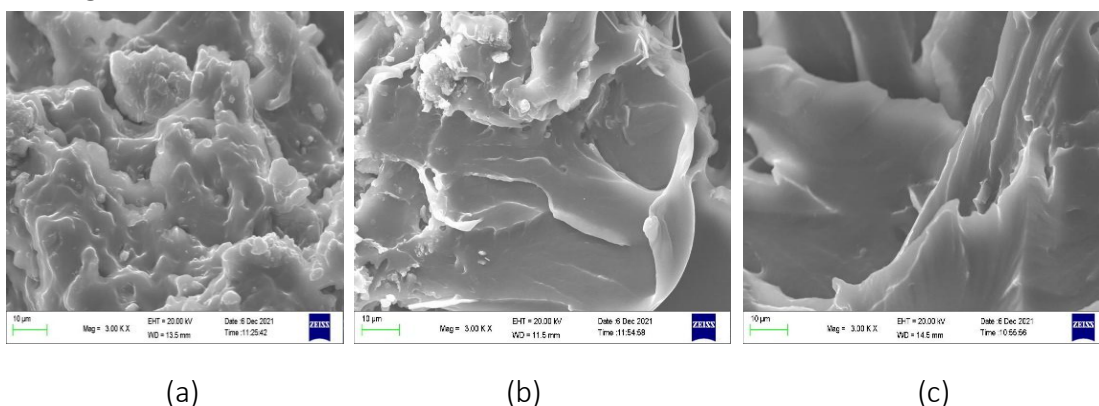
**Figure 2** Elongation at breaks of PVC-g-MA and PVC-g-BA blends



**Figure 3** Modulus elasticity of PVC-g-MA and PVC-g-BA blends

### 3.1.2 Morphology properties

Results of SEM microscopy (magnifications 3000 times) of comonomer modified-PVC blends fracture surfaces (comonomer loadings 10 phr), compared to that of PVC resin as control were shown in Figure 4. It was shown that fracture surface of PVC resin control indicated rough surfaces after fracture (Figure 4a), whereas that of PVC-g-MA (Figure 4b) exhibited more smooth surfaces but with formation of gel due to grafting and crosslinking, which functioned as auto-reinforcements, Tartaglione,(2008). Furthermore, fracture surface of PVC-g-BA blends (Figure 4c) also indicated smooth surfaces but without formation of gel. These evidences supported improved modulus of elasticity of PVC-g-MA blends compared to those of their corresponding PVC-g-BA blends, when the comonomer loading were increased.

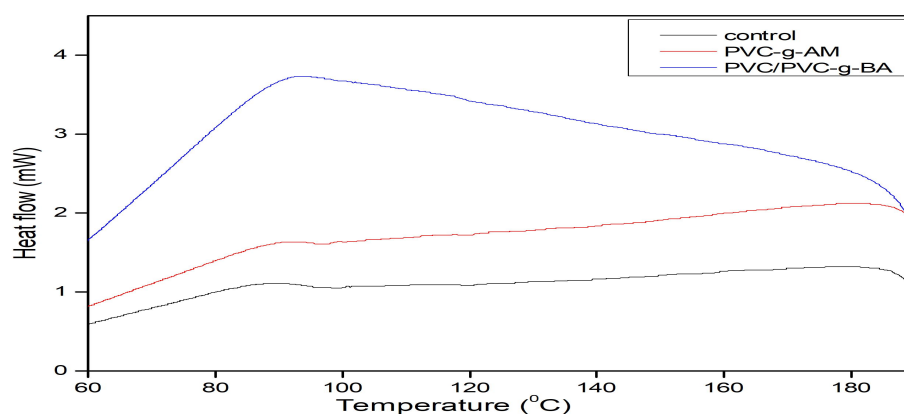


**Figure 4** Micrographs (magnifications 3000 times) of fracture surfaces of: (a) fresh PVC resin (control), (b) PVC-g-A, and (c) PVC-g-BA blends, (comonomers loading 10 phr)

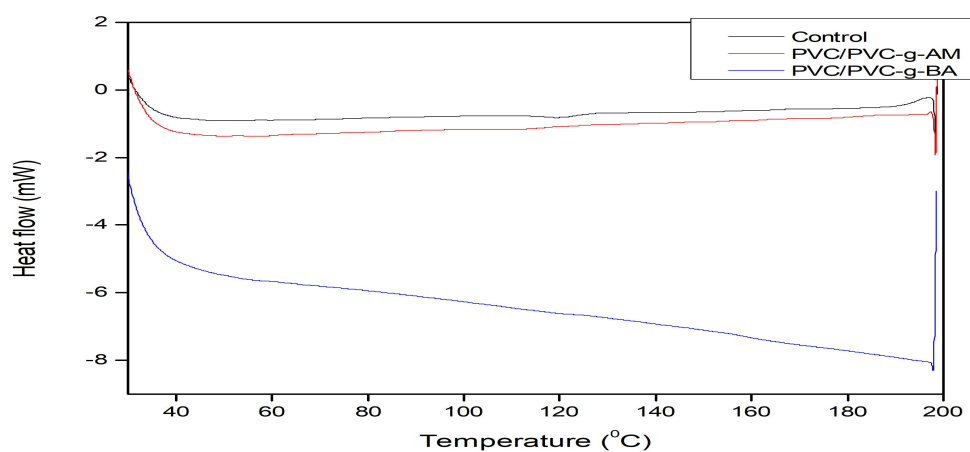


### 3.1.3 DSC analysis

Figures 5 and Table 3 were thermograms and data of DSC analysis (first and second run) of PVC-g-MA and PVC-g-BA (comonomers loading 10 phr) compared to that of fresh PVC (control), (heating range 30°–200°C, heating rate: 10°C/minute). It was shown in Table 3 and Figures 5a and 5b that DSC results of PVCg-MA ad PVC-g-BA samples did not exhibited different melting temperatures ( $T_m$ : 196.48°-198.32°C), however their  $T_g$  and melting heat release were higher compared to that of fresh PVC. These were due to that the modified-PVC blends experienced grafting and crossinking reactions in the presence of peroxide. (Qu et al., 2011)



(a)



(b)

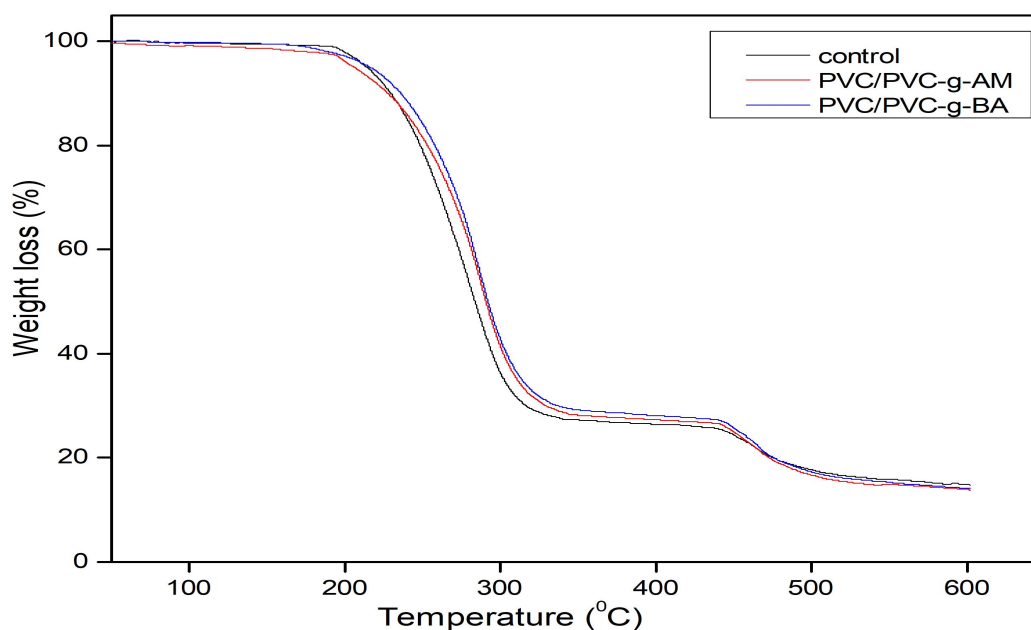
**Figures 5** Thermograms of DSC analysis: (a) First run), (b) Second run, of PVC-g-MA and PVC g-BA compared to that of fresh PVC (control)

**Table 3** Data of DSC of PVC-g-MA and PVC-g-BA (comonomers oading 10 phr) compared to that of fresh PVC (control)

Sample	Tg (°C)	Tm (°C)	Heat flow (J/g)
Fresh PVC	87.48	196.48	-1.01
PVC-g-MA	77.30	198.32	-3.50
PVC-g- BA	93.86	197.86	-8.80

### 3.1.4 TGA analysis

When data of TGA analysis (Figure 6 and Table 4) were analysed it was shown that similar to that of fresh PVC, PVC-g-MA and PVC-g-BA samples also exhibited 2 decompositions which representing decompositions of their amorphous/plastisised and grafted/crosslinked regions. After modifications in the presence of peroxide, their ratio of amorphous region of PVC-g-MA blend decreased (weight loss 71.2-69.4 %) and ratio of the crosslinked region increased (weight loss 7.4-10.8 %). During the second decomposition processes, both PVC-g-MA and PVS-g-BA blends exhibited higher weight loss and less char residue. In other words the modified-PVC blends showed lower thermal stability when compared to that of fresh PVC.



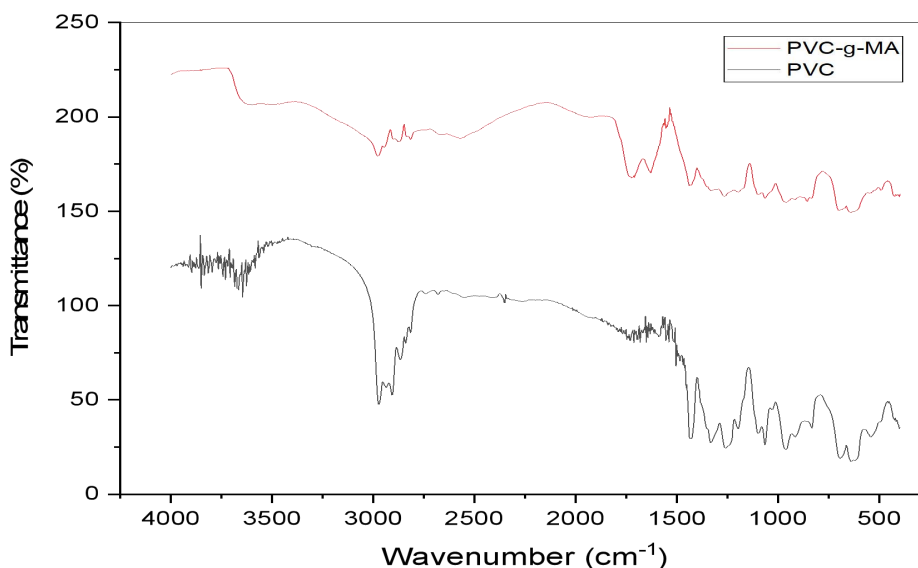
**Figure 6** Thermograms of TGA analysis of PVC-g-MA and PVC-g-BA compared to that of fresh PVC (control)

Sample	Tm (°C)	Decomposition 1		Decomposition 2		
		T (°C)	Weight loss (%)	T (°C)	Weight loss (%)	Char residue (%)
Fresh PVC	195.75	341.52	71.2	492.99	7.4	16.8
PVC-g-MA	191.13	349.85	69.4	516.79	10.8	13.2
PVC-g- BA	176.41	404.87	70.7	488.91	8.7	17.2

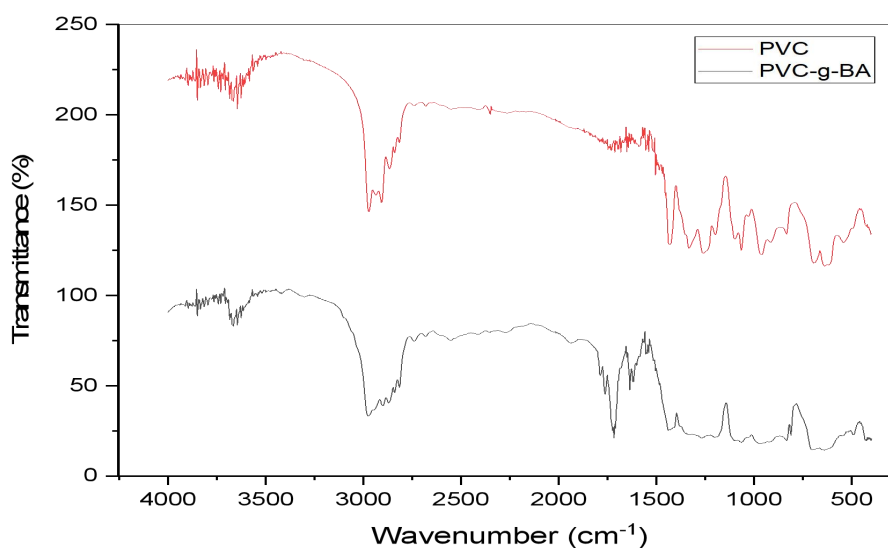
### 3.1.5 Analysis of FTIR spectroscopy

Figures 7 and 8 are FTIR spectra of modified PVC with MA (10 phr) and with BA (10 phr) after washed exhaustively in dichloromethane (DCM), noted as PVC-g-MA and PVC-g-BA, respectively. It was shown in Figure 7 that when compared to that of PVC resins (control), FTIR spectrum of modified PVC with MA (PVC-g-MA) clearly indicated absorption peaks of remaining maleic anhydride group  $[-(\text{CO})-\text{O}-(\text{OC})-]$  at wave numbers 1637.78 dan 1724.38  $\text{cm}^{-1}$ . Similarly, FTIR spectrum of modified PVC with BA (PVC-g-BA

in Figure 8) also showed absorption peaks of remaining buthyl acrylate group  $[-(\text{CO})-\text{O}-(\text{C}_4\text{H}_9)]$  at wave numbers 1627.0 dan 1720.50  $\text{cm}^{-1}$ . These evidences indicated that the MA as well as BA comonomers indeed physico-chemically bound in the modified PVC resins. Mechanisms of the modification reactions were not clear, however it is understood that the presence of BPO as initiator functioned to promote formations of comonomer radicals and PVC macroradicals, which then led for various radical reactions among the radical moieties. And based on results of mechanical, morphology and thermal analysis, the main possible reactions were grafting and crosslinking of comonomers or comonomer homopolymers onto the PVC resins. The MA and BA homopolymers, formed during the radical reactions, were also able to interpenetrate into the PVC macromolecules in THF solution, which then entangled and physically bound into the PVC resins. (Mahendra et al., 2020)



Figures 7 FTIR spectra of modified PVC with maleic anhydride (PVC-g-MA), compared to that of fresh PVC



**Figures 8** FTIR spectra of modified PVC with buthyl acrylate (PVC-g-BA), and washed exhaustively in dichoromethane (DCM), compared to that of fresh PVC

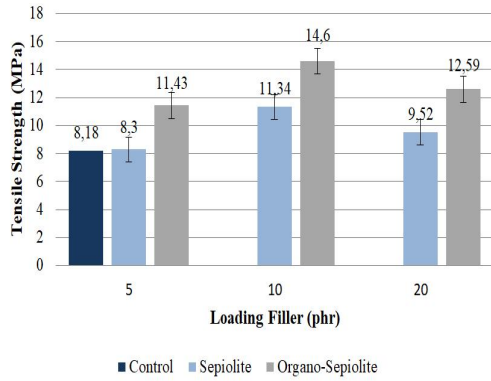
### 3.2 Effects of sepiolites/organo-sepiolites fillers on characteristics of MA/BA-modified PVC blends

Here, sepiolites (Sep) having chemical structure of hydrous magnesium silicates:  $[\text{Si}_{12}\text{O}_3\text{OMg}_8(\text{OH})_4](\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ , their efficiency as reinforcements, compatibilisers and thermal stabilisers in PVC resins were compared with that of cetyltrimethylammonium bromide (CTAB-organo-) modified sepiolites (Osep). The Sep/Osep-filled MA/BA-modified PVC blends were prepared according to Procedure 2.3 at various compositions shown in Table 2, and their characteristics were compared using mechanical testing, morphology study and thermal analysis, as in procedure 2.4

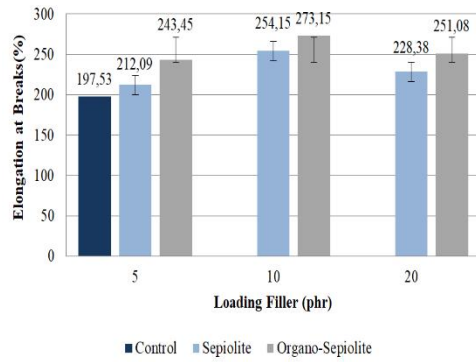
#### 3.2.1 Mechanical properties

Figures 9 showed results of mechanical properties of sepiolites/organo-sepiolites-filled DOP-plastisised MA/BA-modified polyvinylchloride (pPVC-g-MA/BA-Sep/Osep) blends, (comonomer loadings 10 phr, at various fillers loadings). As shown in Figure 9a, when sepiolites loading were increased to 10 phr tensile strengths of pPVC-g-MA-Sep/Osep increased (from 8.18 to 14.6 MPa and to 11.34 MPa, respectively), however when the sepiolites loading were further increased to 20 phr, the tensile strength decreased again (to 11.59 and to 9.52 MPa, respectively). Whereas Figure 9c showed that, their elongation at breaks also increased (197.53 to 273.15 % and to 254.15 %, respectively) at 10 phr loading and then decreased again (to 2.51.08 % and to 228.38 %, respectively) when the fillers

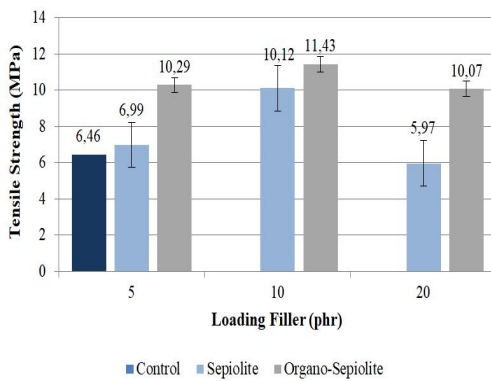
loading increased to 20 %. Furthermore as shown in Figure 9b, in the case of pPVC-g-BA-Sep/Osep blends, when sepiolites loading were increased to 10 phr their tensile strengths increased (from 6.46 to 11.43 MPa and to 10.12 MPa, respectively), however when the sepiolites loading were further increased to 20 phr, the tensile strengths decreased again (to 10.07 and to 5.97 MPa, respectively). Whereas, their elongation at breaks decreased slightly (94.05 to 84.7 % and to 63.4 %, respectively) when the filler loading were increased upto 20% (Figure 9d). These evidences indicated that at lower loading both sepiolites/organo-sepiolites fillers were exfoliated or intercalated, which increased their contact surface area and functioned as reinforcements, Turhan et.al (2013). Whereas at higher loading the fillers tended to saturate and experienced agglomeration, which reduce their contact surface area and decreased their tensile strengths and elongation at breaks. When compared to those of their corresponding sepiolites-filled, the organo-sepiolites filled always exhibited higher tensile strengths and elongation at breaks, which due to better compatibility of the organo (CTAB)-sepiolites in the pPVC-g-MA/BA blends. The CTAB-covered of organo-sepiolites fillers possessed reduced surface energy due to the hydrophilic part (ammonium bromide group) of the CTAB interacted strongly on to the surfaces of hydrous sepiolites fillers, whereas the hydrophobic part (cethyl group) interacted with the pPVC-MA/BA matrices. However, compatibility of both sepiolites/organo-sepiolites fillers were better in pPVC-g-MA than in pPVC-g-BA matrices, because of the anhydride (-O-CO-O-) groups of MA chemically interacted to form -O-CO-OH and H-O- groups, whereas the carboxylic (-CO-OH) groups of BA only physically (through hydrogen bonding) interacted with the hydrous sepiolites fillers, Wirjosentono et.al (2019). These were also supported by increased of their modulus of elasticity in the case of pPVC-g-MA blends (Figure 9e) when compare to those of their corresponding pPVC-g-BA blends (Figure 9f).



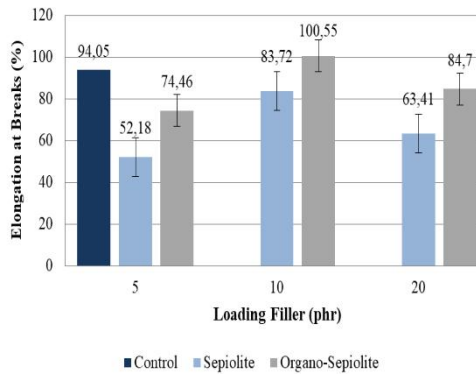
(a)



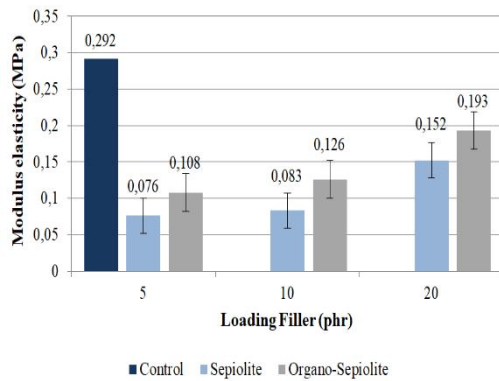
(b)



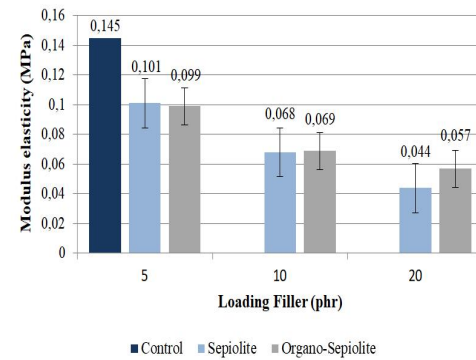
(c)



(d)



(e)

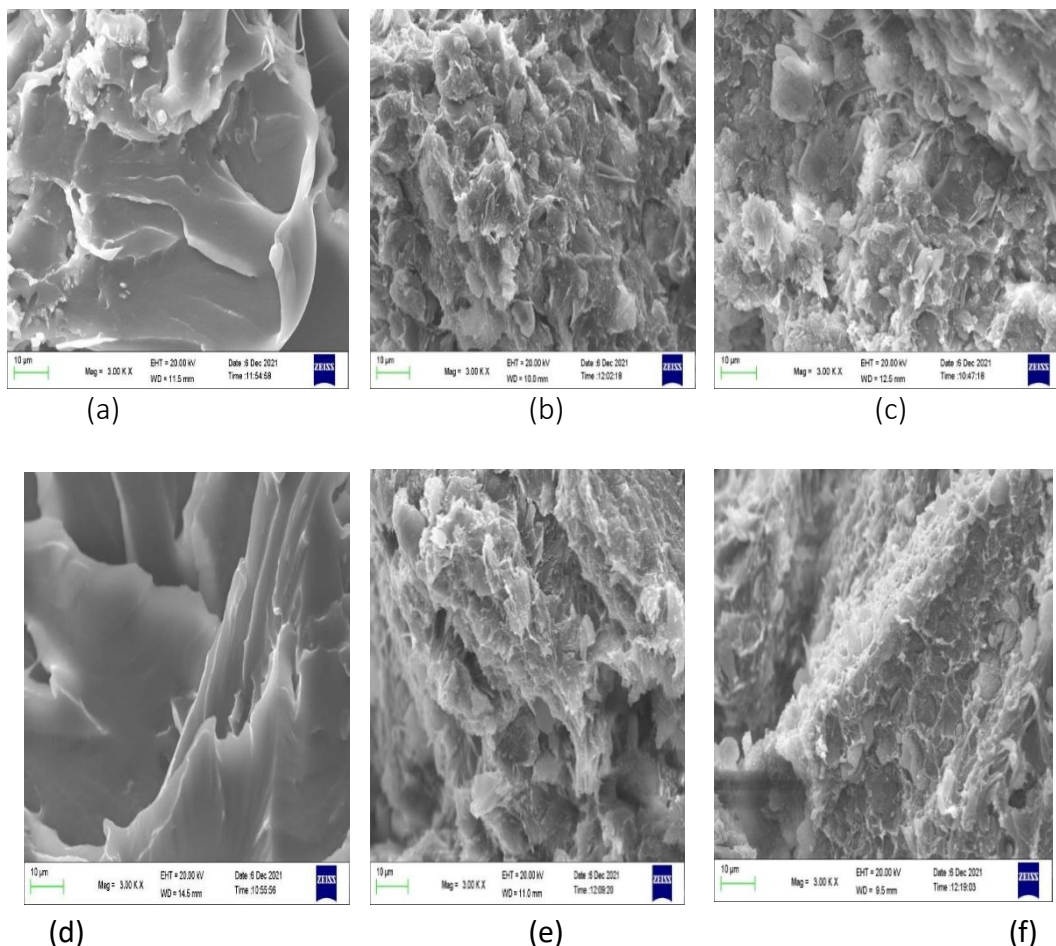


(f)

Figures 9. Tensile strengths, elongation at breaks, and modulus of elasticities of DOP-plasticised Sep/Osep-filled pPVC-g-MA (9a, 9c, and 9e, respectively), and of DOP-plasticised Sep/Osep-filled pPVC-g-BA (9b, 9d, and 9f, respectively) blends, (comonomer loadings 10 phr, at various fillers loadings)

### 3.2.2 Morphology properties

Figures 10 were SEM micrographs (magnifications 3000 times) of fracture surfaces of DOP-plastisised Sep/Osep-filled pPVC-g-MA/BA blends (fillers and comonomers loadings 10 phr). As shown in Figures 10a and 10d, SEM micrographs of fracture surfaces of DOP-plastisised PVC-g-MA/BA (control), respectively, they exhibited smooth fracture surfaces due to plastisising effect of DOP (30 phr). In the case of Sep/Osep-filled (at optimum 10 phr loadings) in pPVC-g-MA blends, the fracture surfaces showed finely distributed sepiolites particles and rougher fracture surfaces (Figure 10b, sepiolites-filled), and even more finely distributed organo-sepiolites particles and smaller and sharper size of fracture roughness (Figure 10c). In the case of Sep/Osep-filled (at optimum 10 phr loadings) in pPVC-g-BA blends (Figures 10e and 10f), their fracture surfaces also exhibited similar trends with those of their corresponding pPVC-g-MA blends. These were due to better compatibility of organo-sepiolites compared to its original sepiolites in both the pPVC-g-MA/BA matrices. (Nasution et al., 2020)

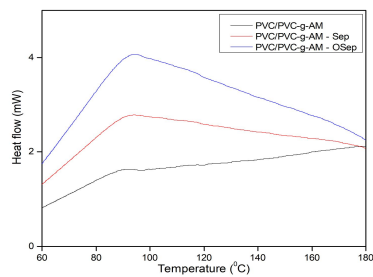


Figures 10. SEM micrographs (magnifications 3000 times) of fracture surfaces of: (a) DOP-plastisised pPVC-g-MA, (b) containing sepiolites 10 phr, (c) containing organo-sepiolites 10 phr, and (d) DOP-plastisised pPVC-g-BA, (e) containing sepiolites 10 phr, (f) containing organo-sepiolites 10 phr.

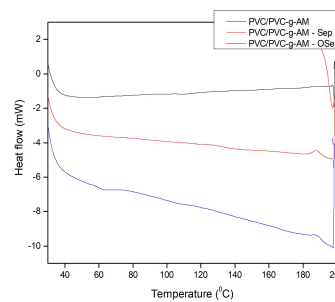
### 3.2.3 DSC analysis

Main objectives in thermal analysis were to estimate not only thermal stability, but also the effects of temperatures on characteristics during utilisations and service-life of the PVC

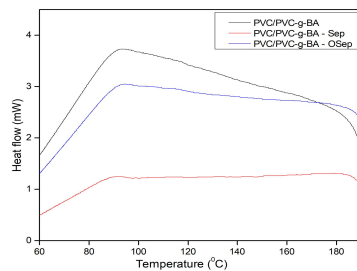
blends as engineering thermoplaastics. These were studied by measuring glass transition and melting temperatures for amorphous/plastisised and grafted/crosslinked regions of the PVC samples using DSC technique. Thermographs and data of DSC analysis of DOP-plastisised Sep/Osep-filled pPVC-g-MA/BA blends (comonomers and fillers loadings 10 phr) were shown in Figures 11 and Table 5. It was shown that DSC results of pPVCg-MA/BA samples did not exhibited different melting temperatures ( $T_m$ : 197.64° to 198.39°C), however their  $T_g$  and melting heat release were higher (-3.50 to -9.96 J/g) compared to that of pPVC-g-MA. These indicated that the sepiolites and organo-sepiolites fillers were well interacted physico-chemically (grafted/crosslinked) in the MA/BA-modified Sep/Osep-filled pPVC blends and therefore required higher heat energy to decompose the blends. (Saragih et al., 2020)



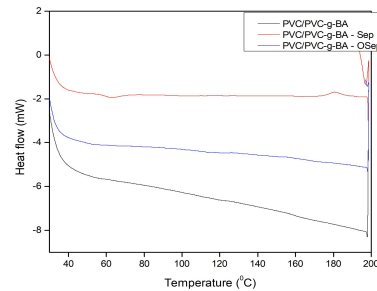
(a) pPVC-g-MA-Sep/Osep, first run



(b) pPVC-g-MA-Sep/Osep, second run



(c) pPVC-g-BA-Sep/Osep, first run



(d) pPVC-g-BA-Sep/Osep, second run

**Table 5** DSC data of pPVC-g-MA/BA-Sep/Osep blends

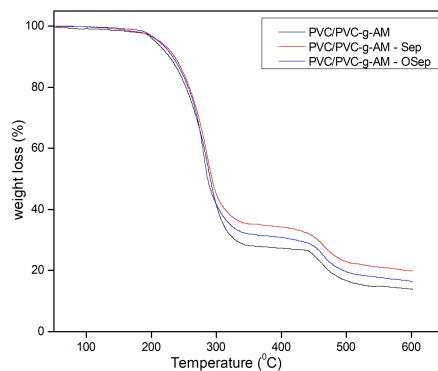
Sampel	$T_g$ (°C)	$T_m$ (°C)	Heat flow (J/g)
pPVC-g-MA	77.30	198.32	-3.50
pPVC-g-MA-Sep	94.26	198.06	-2.73
pPVC-g-MA-Osep	94.47	197.64	-9.96



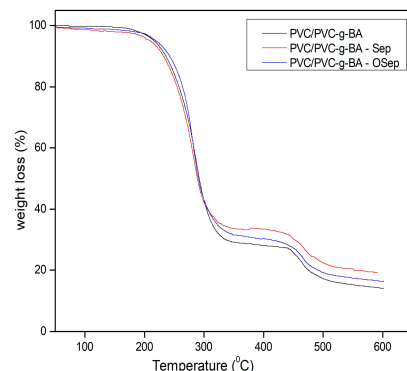
pPVC-g-BA	93.86	197.86	-8.80
pPVC-g-BA-Sep	91.88	198.39	-4.56
pPVC-g-BA-Osep	94.56	198.09	-8.89

### 3.2.4 TGA analysis

Here, thermal stability of the PVC samples were estimated by measuring decomposition temperatures, amount of weight loss and char residue after total decompositions. When thermographs and data of TGA analysis (Figures 12 and Table 6) were scrutinized it was shown that similar to that of pPVC-g-MA/BA, all pPVC-g-MA/BA-Sep/Osep samples also exhibited 2 steps decompositions processes. The first (range temperatures 344.6° to 433.85°C) represented decompositions of their plastisised/amorphous regions, whereas the second (range temperatures 488.91° to 520.94°C) represented the grafted/crosslinked of the Sep/Osep-filled regions. It was exhibited from Table 6 that during the first decomposition steps, amount of weight losses showed no substantial differences for all samples (weight losses: 62.4-70.7 %). However, during the second decomposition processes that in the case of Sep/Osep-filled samples the amount of weight loss were decreased (10.8-9.2 %) and amount of char residue were increased (13.2-21.1 %) than those of their corresponding control without the fillers. These revealed that the hydrous magnesium silicate sepiolites/organo-sepiolites fillers functioned as thermal stabilisers for pPVC-g-MA/BA blends, by formation of char residues which covered surfaces and inhibited oxygen diffusion into the decomposing pPVC blends. (Xu et al., 2013). However, the organo-sepiolites fillers possessed lower thermal stabilizer properties that those of their origin sepiolites fillers, since the formers were covered with CTAB films which inhibited direct surface contacts of the fillers with the decomposing pPVC blends.



(a) pPVC-g-AM-Sep/Osep



(b) pPVC-g-BA-Sep/Osep

**Figure 12** DSC thermographs of pPVC-g-MA-Sep/Osep dan pPVC-g-BA-Sep/Osep blends

**Table 6** TGA data of PVC-g-AM-Sep dan PVC-g-AM-Osep

Sample	Tm (°C)	Decomposition 1		Decomposition 2		
		T (°C)	Weight loss (%)	T (°C)	Weight loss (%)	Char residue (%)
pPVC-g-MA	191.13	349.85	69.4	516.79	10.8	13.2
pPVC-g-MA-Sep	186.03	344.6	62.4	503.3	9.6	20.6
pPVC-g-MA-Osep	182.88	347.75	66.5	512.62	9.2	17.4
pPVC-g-BA	176.41	404.87	70.7	488.91	8.7	17.2
pPVC-g-BA-Sep	186.93	433.85	64.8	520.94	11.2	21.1
pPVC-g-BA-Osep	203.68	355.07	65.5	520.93	9.1	18.3

#### 4. Conclusions

The main possible reactions in the modification procedures were grafting and crosslinking of MA and BA comonomers or comonomer homopolymers onto the PVC resins. The MA and BA homopolymers were also able to interpenetrate into the PVC macromolecules, which then entangled and physically bound into the PVC resins. When compared to those of their corresponding original sepiolites, the organo-sepiolites promoted higher tensile strengths and elongation at breaks, due to better compatibility of the later in the pPVC-g-MA/BA blends. Modification with MA and BA comonomers increased compatibility of sepiolites/organo-sepiolites-filled, and therefore improved morphology properties of pPVC-g-MA/BA-Sep/Osep blends. During decomposition processes the sepiolites and organo-sepiolites fillers were well interacted physico-chemically (grafted/crosslinked) in the MA/BA-modified Sep/Osep-filled pPVC blends and therefore required higher heat energy to decompose the blends. The hydrous magnesium silicate sepiolites/organo-sepiolites fillers functioned as thermal stabilisers for pPVC-g-MA/BA blends, by formation of char residues which covered surfaces and inhibited oxygen diffusion into the decomposing pPVC blends, although the organo-sepiolites fillers possessed lower thermal stabilizer properties than those of their origin sepiolites fillers.

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