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Advancement of aliphatic polycarbonates with nanoclay addition: An overview

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Abstract

Aliphatic polycarbonates are considered as newly developed biodegradable polymer, which results from a sustainable copolymerization of epoxides and carbon dioxide (CO_2) process. These aliphatic carbonates have weak properties in terms of thermal stability and mechanical properties, due to its carbon structure flexibility, hence causing limitation to its applications. Up to date, studies on aliphatic polycarbonates are progressively conducted to maximize its opportunity as an alternative nanocomposite. This review was carried out to provide insights on the progression in producing aliphatic polycarbonates by incorporating various type of fillers to enhance physicochemical, thermal and mechanical properties of aliphatic polycarbonates. The results revealed that a blend of aliphatic polycarbonates/clay nanocomposites with low clay content up to 10 wt.% displayed improved glass transition temperature and thermal degradation in comparison with the pure one. The improved thermal stability was due to the nanoparticle's dispersion into matrix of aliphatic polycarbonates. The mechanical properties such as Young's Modulus and tensile strength of aliphatic polycarbonates were also improved with addition of nanoclay. The improvement of thermal and mechanical properties of aliphatic polycarbonates at low content of nanoclay proves that the addition of nanoclay into polymer matrix is a promising technique to design the properties of aliphatic polycarbonates particularly for the coating application as water and oxygen barrier film.

1.0 Introduction

Pollution from packaging material has become massive worldwide environmental issues. Nowadays, there are numerous of ways made to produce innovative biodegradable materials to substitute traditional polymer which is nondegradable to solve this issue. Aliphatic polycarbonates are new thermoplastic polymer which own biodegradable properties and lure much attention from many researchers (Inoue et al., 1969; Darensbourg & Holtcamp, 1995; Super & Beckman, 1997; Tan & Hsu, 1997; Meng et al., 2010). Aliphatic polycarbonates are made up from the copolymerization of carbon dioxide (CO_2) and epoxide using catalyst (Inoue et al., 1969). The usage of carbon dioxide is attractive because its availability, low cost, abundance, and nontoxicity (Taherimehr & Pescarmona, 2014). Thus, carbon dioxide content in the atmosphere may be reduced effectively and the global warming issues according to Global Energy & CO_2 Status Report 2017 published in 2018 are potentially mitigated. The widely used polymers such as the thermoplastics in the market (Michel, 2016) are possibly substituting with these aliphatic polycarbonates.

Aliphatic polycarbonate is new thermoplastic polymer that first synthesized from epoxide and carbon dioxide in year 1969 by Inoue. Synthesis of aliphatic polycarbonate from epoxide and carbon dioxide is shown in Fig. 1.

These polycarbonates are biodegradable polymers which result from its aliphatic structure. Aliphatic polycarbonate has low oxygen permeability oxygen which is suitable in food packaging material (Sugimoto & Inoue, 2004). Aliphatic polycarbonate also can
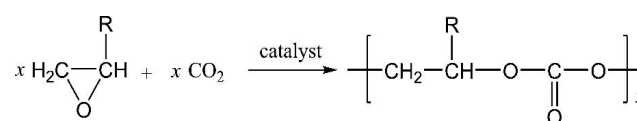

Fig. 1: Synthesis of Aliphatic Polycarbonates from Epoxides and CO_2: R = Side Chain (Sasanuma & Takahashi, 2017).

undergo quick enzyme-medicated bio-absorption in vivo, thus it can be applied to control the drugs release as its exclusive depends on the polymer degradation (Acemoglu, 1997). The other applications of aliphatic polycarbonate are as cost-effective additives to enhance printability and processability of polyolefins and decrease the shrinkage in calendared polypropylene. Besides, these polymers also use to enhance the mechanical properties of styrene butadiene rubber and for creating interpenetrating networks (IPNs) with other polymers (Sudhir et al., 2009). However, aliphatic polycarbonates have many flaws such as non-crystallizable, weaker processing stability, poor mechanical properties, and poor thermal stability due to the flexible carbonate groups in backbone chains which cause limitation in its application (Meijun, 2011).

The aliphatic polycarbonates have been modified to improve its physicochemical and mechanical properties by using nanoparticles. This is vital to maintain the unique physical and mechanical properties, and biodegradable properties of aliphatic polycarbonates, so the polymers could be used in various applications. Nanoparticle such as organoclay shows exceptional advancements in physical and thermal properties of aliphatic polycarbonate at very small filler content. Organoclay or nanoclay is produced from the layered silicates which pass through ion exchange process (Hasmukh et al., 2006). The organoclay also cheaper and more convenience compares to other common composites hybrid typed fillers, such titanium dioxide (TiO_2) and silica oxide (SiO_2). This study is carried out to reveal the potential of clay in modifying the thermal and mechanical properties of the aliphatic polycarbonates by focusing on different methods of preparation for the aliphatic polycarbonates/clay nanocomposites.

2.0 Fundamental of aliphatic polycarbonate

Aliphatic polycarbonate is different from the conventional polycarbonate that is produced from bisphenol A, whereas the aliphatic polycarbonate is produced from the copolymerization of epoxide molecules and carbon dioxide. The differences between the synthesis route of aliphatic polycarbonate and conventional polycarbonate respectively are shown in Fig.2.

Remarkable attention by researchers on the polycarbonate production due to huge concern for the global warming issues (Cui et al., 2019; Shuxian et al., 2019). Hence, the CO_2 fixation will be happened by absorbing the carbon dioxide released by the natural gas, petroleum and coal combustion using the basic polymer such as polyethylene oxide and its derivatives may produce polyethylene carbonate from the collected gas (Sasanuma & Takahashi, 2017).

3.0 Aliphatic polycarbonate properties

3.1 Glass transition temperature, T_g of aliphatic carbonate

Glass transition temperature (T_g) of linear chain aliphatic polycarbonate decreases starting from poly(ethylene carbonate) as the side-chain length in the repeat unit increases, except for the poly(propylene carbonate) as shown in Table 1. T_g value for poly(propylene carbonate) is higher compare the other aliphatic polycarbonate because –CH_3 side group which make the chain stiffer than poly(ethylene carbonate) which only contain H atom on the side group, thus increasing glass transition temperature. For other longer linear chain aliphatic polycarbonates, the glass transition decreases due to the polymer polar chains with some dipolar interactions contributing to the bonding, which appears that the longer flexible side chains are pushing the main chains apart and lowering the glass transition temperature through that mechanism. For poly(cyclohexene carbonate) the T_g is higher compared to the linear chain aliphatic polycarbonate because it has higher chain stiffness results from the stiff cyclohexene ring (Sudhir et al., 2009).
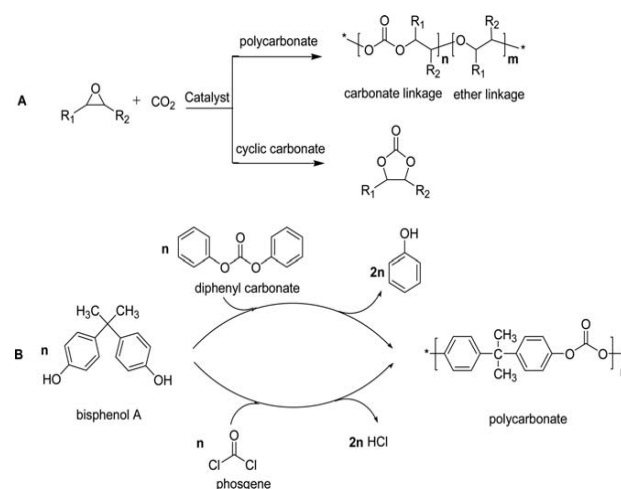

Fig. 2: (A) Synthesis of aliphatic polycarbonate from copolymerization of epoxide and CO_2. (B) Synthesis of conventional polycarbonate from bisphenol A (Taherimehr & Pescarmona, (2014).

Table 1: Glass transition temperature (T_g) of aliphatic polycarbonate obtained from DSC (Sudhir et al., 2009).

Aliphatic Polycarbonate	DSC T_g (°C)	
	Range	Inflection Point
Poly(ethylene carbonate)	8 to 12	10
Poly(propylene carbonate)	22 o 30	28
Poly(linear pentene carbonate)	−6 to −1	−4
Poly(linear hexane carbonate)	−12 to −7	−10
Poly(linear octene carbonate)	−8 to −12	−16
Poly(cyclohexene carbonate)	99 to 111	105

Table 2: Initial decomposition temperatures (IDT) of aliphatic polycarbonates in air and nitrogen (Sudhir et al., 2009).

Aliphatic Polycarbonate	IDT (°C)	
	Air	Nitrogen
Poly(ethylene carbonate)	217	232
Poly(propylene carbonate)	235	238
Poly(linear pentene carbonate)	246	270
Poly(linear hexane carbonate)	250	280
Poly(linear octene carbonate)	257	268
Poly(cyclohexene carbonate)	282	290

3.2 Thermal degradation of aliphatic polycarbonate

The thermal degradation of aliphatic polycarbonate is lower (Lu et al., 2005; Phillips et al. 2016) compared to those chain-reaction polymers such as polyethylene and polypropylene. The initial thermal degradation of aliphatic polycarbonate is tabulated in Table 2. Thermal degradation of these aliphatic polycarbonates is higher in nitrogen atmosphere as compared in the air atmosphere due to the presence of oxygen in air that effects the rate of degradation of the polymers. The initial decomposition temperature (IDT) of aliphatic polycarbonate increases with the increase in number of hydrocarbon content in the polymer. This indicate that the degradation temperature is affected by the chemical structure of the polymer. Based on Table 2, poly(cyclohexene carbonate) has the highest IDT value in comparison with the other aliphatic polycarbonate because it has stiff polymer chain. Thus, hydrocarbon content and stiffness of molecular backbone will affect the thermal degradation of these polymers (Sudhir et al., 2009).

3.3 Mechanical properties of aliphatic polycarbonate

The mechanical properties of aliphatic polycarbonates depend on the glass-transition temperature and the polymer structure. The mechanical properties of linear poly(pentene carbonate), linear poly(hexene carbonate), and linear poly(octene carbonate) which have T_g value less than zero are fragile in room temperature, thus the tensile test on these polymers cannot be carried out (Sudhir et al., 2009). Table 3 show the average mechanical properties of the remaining aliphatic polycarbonates which are poly(ethylene carbonate), poly(propylene carbonate) and poly(cyclohexene carbonate).

As shown in Table 3, the elastic modulus of polymer elastomer from the aliphatic polycarbonates decreased from poly(cyclohexene carbonate) to poly(propylene carbonate) with the same order as their T_g values. Poly(ethylene carbonate) has strain at break more than 600% which cause it to behave as elastomeric material whereas, poly(cyclohexene carbonate) has strain at break less than 1% indicating this polymer is brittle (Sudhir et al., 2009). Having instability behaviour for the mechanical properties that due to its flexibility of each aliphatic polycarbonate making this material credentials to limited various applications.

3.4 Applications and limitation aliphatic polycarbonate

Aliphatic polycarbonates have been used in broad range of applications. Poly(propylene carbonate) has been applied for binders, brazing pastes and solutions, propellants and diamond cutting tools. Based on the biodegradability and thermoplastic properties of these aliphatic polycarbonates, these polymers have been applied in biomedical, packaging material and binder resins (Zhang et al., 2006; Sher, 2009). In biomedical,

Table 3: Mechanical properties of aliphatic polycarbonate (Sudhir et al., 2009).

Aliphatic Polycarbonate	Modulus (MPa)	Tensile Strength (MPa)	Strain at break (%)
Poly(ethylene carbonate)	3-8	-	>600
Poly(propylene carbonate)	212	9	8
Poly(cyclohexane carbonate)	2460	11.8	0.5

poly(ethylene carbonate) is used as drug carrier because of its unique mechanism during degradation and the polymer properties as drug carrier. Poly(ethylene carbonate) matrix protect well drugs as there is no developing swelling occurred (Georg et al., 2001). The drug release from this polymer matrices in the organisms was depending by the surface erosion, which causing 1:1 relationship between polymer mass loss and drug release. Furthermore, aliphatic polycarbonates also can be applied in ion-conductive solid polymer electrolytes (SPEs). Mixtures of polar polymer and metal salts contains in SPEs. In SPEs, the aliphatic polycarbonate will be the polymer host. SPEs is vital technology in broadening the use of renewable energies by assisting energy story and electric vehicles (EVs) (Kento & Tominaga, 2016; Zhenguang et al., 2018; Tominaga et al., 2019).

Work on poly(propylene carbonate), PPC for the composites (Li et al., 2003; Ge et al., 2004; Ge et al., 2005, Lu et al., 2006, Zeng et al. 2011, Ohlendorf et al., 2017) and for the PPC blends (Jiao et al., 2007; Wang et al., 2007; Zhang et al., 2008; Pang et al., 2008; Zhao, et al., 2011; Lagaron et al., 2011; Chen et al., 2013; Cheng et al., 2013) have well established. Recently, poly(ethylene carbonate), PEC has been introduced as modifier to the poly(lactic acid), in which the flexibility, the tensile toughness, the hydrolysis of the poly(lactic acid) have increased with 40 wt.% of PEC (Ramlee & Tominaga, 2018; Ramlee & Tominaga, 2019; Ramlee & Tominaga, 2019).

4.0 Preparation of aliphatic polycarbonate with nanoclay

Based on several findings, the methods to prepare aliphatic polycarbonate with nanoclay could be categorized into two which the melt polymer intercalation and the direct solution intercalation (Oliveira & Machado, 2013). Direct solution intercalation or solution blending method can be defined as a process of blending polymer and inorganic powder using as solvent in which the polymer is soluble. The nanofiller disperses well into polymer matrices through this method (Kotal & Anil, 2015). The method of solution blending is shown in Fig. 3. Next, melt polymer intercalation or melt blending method is defined as process of direct mixing of the filler into a polymer matrix in melt blending. This method is shown is Fig. 4. Besides, this method also can reduce the time for nanocomposites fabrication (Zhu et al., 2005).
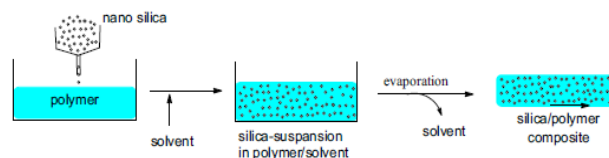

Fig. 3: Solution blending method to prepare polymer/nanofiller composites (Kotal & Anil, 2015).
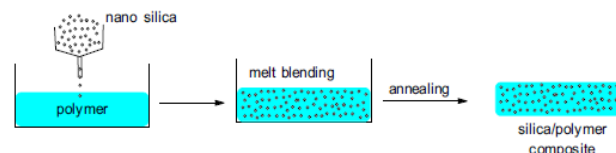

Fig. 4: Melt blending method to prepare polymer/nanofiller composites (Kotal & Anil, 2015).

Table 4: Method of preparation poly(propylene carbonate) and nanoclay from recent studies.

Type of method preparation	Nanoclay	Authors
Solution intercalation	Montmorillonite	Shi & Gan (2007)
	Cloisite 20B	Sher (2009)
Melt blending	Organo-vermiculite	Xu et al., (2005)
	Montmorillonite	Xu et al., (2006)
	Organo-modified rectorite (OREC)	Wan et al., (2007)

To support these findings, Table 4 shows the recent work on the preparation method for aliphatic poly(propylene carbonate)/nanoclay composites. Based on Table 4, the common methods of preparing aliphatic polycarbonate and nanoclay are melt blending and solution intercalation. The melt blending method showed that the intercalation-exfoliated structure of the aliphatic polycarbonate/clay nanocomposites was achieved (Zhu et al., 2006), whereas the solution intercalation method showed the nanocomposites only has an intercalated structure (Shi & Gan, 2007). This show the nanoclay from both methods applicable to introduced intercalated nanoclay structure into the polymer structure.

A few problems were reported such as thermal degradation of aliphatic polycarbonate and loss of mechanical property could happen for this melt-blending process (Shi & Gan, 2007). However, the nanocomposites result from the melt blending continuing displayed better mechanical properties such as good toughness and high tensile strength as compared to the solution intercalation method as reported by Fukushima & Inagaki, (1987) based on the synthesis of an intercalated compound of montmorillonite and with 6-Polyamide.

5.0 Modification of aliphatic polycarbonate with nanoclay addition

Aliphatic polycarbonate/clay nanocomposites have unique properties such as the low water adsorption capacity, display increment of tensile modulus, decrease gas permeability and increased thermal stability compare to conventional composites (Sher, 2009). The enhancement of the composites physicochemical, thermal, and mechanical property depends on the quantity of the clay loading and the degree of dispersion of aluminosilicate layers in the polymer matrix. The physicochemical, thermal, and mechanical properties of aliphatic polycarbonate/clay nanocomposites display improvement at small clay fillings between 0.5 to 5 wt.% compare to conventional clay-filled composites in size of micro and macro composites (Sher, 2009). Nevertheless, the aliphatic polycarbonate displayed deteriorated properties at high amount of clay content such as increment in density and loss of tenacity because of the incompatibility of interfacial between inorganic filler and organic polymer. At high content of filler, aggregation is forming and these aggerates will act as stress concentration and lowered the mechanical properties. There are various studies on poly(propylene carbonate) (PPC)/clay composites. The influence of glass transition temperature, thermal stability, and mechanical properties with the introductory of nanoclay to PPC prior to the intercalated structure nanoclay that is formed in the nanocomposites are discussed in the next section.

5.1 Glass transition temperature, T_g of aliphatic polycarbonate with nanoclay

The glass transition temperature of aliphatic polycarbonate, T_g is low and has limit its applications. However, the aliphatic polycarbonate such as poly(propylene carbonate) (PPC) show improved T_g value with low content of nanoclay. The T_g values of poly(propylene carbonate) (PPC) at different content of nanoclay are tabulated in Table 5. Based on Table 5, the glass transition temperature of PPC/organically modified montmorillonite (OMMT) nanocomposites show increment at low nanoclay content. The highest T_g value is 35.7°C reported by Xu et al., (2006) at OMMT content of 8 wt.% which this T_g value is 2.4°C higher than the pure PPC. Where, the T_g value increased significantly as reported by Shi & Gan (2007) with only 4 wt.% of OMMT content, giving

Table 5: Tg value of PPC at different content of nanoclay (Xu et al., 2006; Shi & Gan 2007).

(Xu et al., 2006)		(Shi & Gan (2007))	
Melt blending		**Solution intercalation**	
Specimen	T_g (°C)	Specimen	T_g (°C)
Pure PPC	33.3	Pure PPC	21.0
PPC/2% OMMT	34.4	PPC/ 2% OMMT	30.0
PPC/4% OMMT	33.8	PPC/4% OMMT	32.0
PPC/6% OMMT	33.8	PPC/6% OMMT	34.0
PPC/8% OMMT	35.7	PPC/8% OMMT	32.0

34% increment with 13°C, in comparison with the pure PPC. The improved T_g value is due to the strong interaction between the polymer and the nano-dispersed silicate layers, which restricts the segmental motion of PPC molecular chains (Xu et al., 2006). Besides, PPC/nanoclay composites was accomplished to be prepared by solution intercalation as reported by Shi & Gan (2007) with high content of nanoclay to more than 8 wt.% in comparison with the one prepares by the melt blending (Xu et al., 2006). High content of nanoclay did not give a significantly effect to the change for T_g when it was prepared by the melt-blending method.

This may result from the different method PPC/OMMT nanocomposites preparation. Preparation of PPC/clay nanocomposites by solution intercalation method showed highest increment of T_g value from the pure PPC in comparison with the one prepared by the melt-blending (Xu et al., 2006; Shi & Gan, 2007). The increment of glass transition temperature at low content of nanoclay proves that the addition of nanoclay into the aliphatic polycarbonate matrix is an efficient way to increase the thermal stability of PPC.

5.2 Thermal stability of aliphatic polycarbonate with nanoclay

Evidently, added nanoclay to aliphatic polycarbonate has influenced the carbonate group on the aliphatic carbonate back bone chain flexibility, which the T_g is shifting prior to its addition. Hence, the thermal properties, such as thermal degradation of these nanocomposites are also influenced significantly. Fast thermal decomposition of PPC as shown in Fig. 5
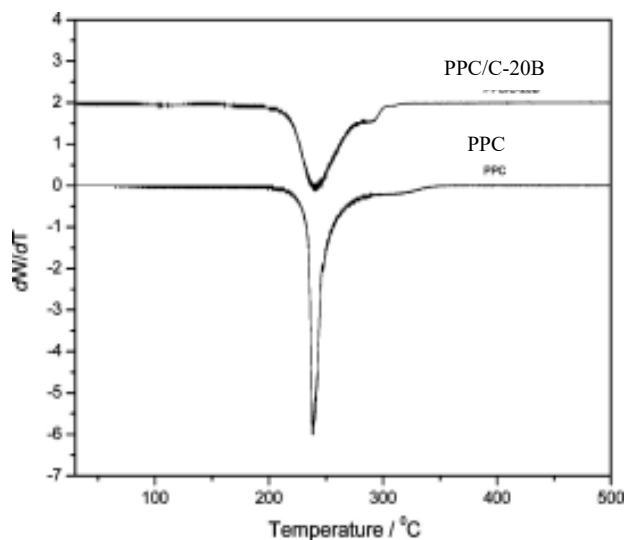
Fig. 1: DTG curves of PPC/C-20B composites and PPC (Sher, 2009).

Fig. 6: TGA curves of pure PPC and the PPC/OMMT nanocomposites with various OMMT contents (Xu et al., 2006).

was significantly reduced with the introduction of wt. % of organo-clay nanohybrid denoted as (C-20B) (Sher, 2009).

The clay act as a superior insulator inside the polymer matrix which result to the increasing thermal stability. The uniform dispersion of silicate layers in PPC matrix led to the difficulty in heat conduction and playing role as a mass transport barrier to the volatile products which create during decomposition. The role of the silicate layers in the PPC matrix will result in lag, wide and coarse peaks during decomposition (Sher, 2009). Therefore, the presence of clay has delayed the decomposition rate for the pure PPC with the evident of broader DTG curve for PPC/C-20B nanocomposites in comparison with the sharp DTG curve for the pure PPC.

TGA curves for PPC/organically modified montmorillonite (OMMT) nanocomposites are shown in Fig. 6. PPC with addition (OMMT) nanoclay also displays better in thermal decomposition. The composites started to degrade at higher temperature which around 270 °C with the OMMT addition at less of 6 wt.% nanoclay in comparison with the pure PPC, which the degradation is started earlier around 242 °C. This situation is due to the shielding effect of OMMT layer that displayed clear barrier effect to stop the evaporation of the small molecules generated during the thermal decomposition and effectively limited the progress of decomposition of PPC. In contrast to PPC, the amorphous PPC became more stable due the well-dispersed of OMMT in PPC matrix. However, the PPC/20% OMMT which has high content of OMMT, displaying the lowest thermal stability in comparison
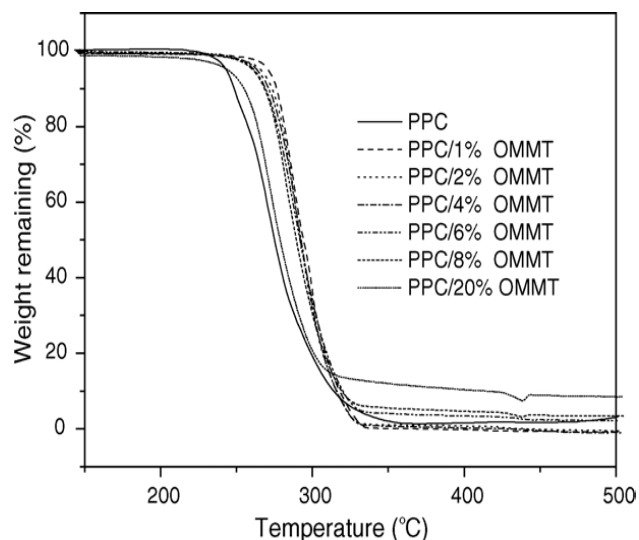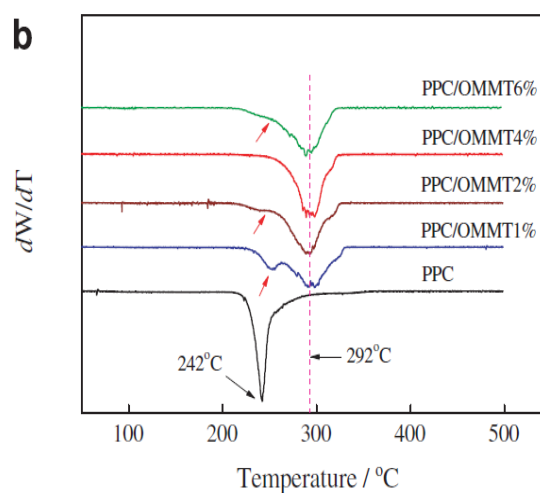

Fig. 7: DTG curves of PPC and PPC/OMMT nanocomposites with different OMMT contents (Shi & Gan, 2007).

with other PPC/OMMT compositions. This poor thermal stability might be due to organic ammonium compounds within the OMMT (Xu et al., 2006) that causing less thermal stability for these nanocomposites.

Thermal decomposition characteristics of a polymer are affected by heating rate, surrounding atmosphere, sample weight and shape (Shi & Gan, 2007). Based on the DTG curve in Fig. 7, the fastest thermal decomposition temperatures after the addition of OMMT nanoclay are increased by 50°C relative to the pure PPC. The DTG curve of the PPC/OMMT nanocomposites show in Fig. 7 also became wider coarser compared with the pure PPC. This is result from the incorporation of the nanoclay into the aliphatic polycarbonate matrix which act as a superior

insulator. The enhancement of thermal stability of the nanocomposites shows that the decomposition temperature of the nanocomposites increased as compared to the pure aliphatic polycarbonate.

5.3 Mechanical properties of aliphatic polycarbonate with nanoclay

The addition of nanoclay show improvement in mechanical properties of aliphatic polycarbonate as shown in Fig. 8, where the nanocomposites of PPC and OMMT display better tensile strength and Young's Modulus compare to the pure PCC. This is resulted from the nano-scale dispersion of OMMT in PPC matrix. The strong interfacial interaction of OMMT and PPC matrix, and the excellent properties of nanoclay cause to the improvement of mechanical properties of the nanocomposites.

However, at higher nanoclay content, some silicate layers start to aggregate. The interfacial area of aliphatic polycarbonate and silicate layer will reduce
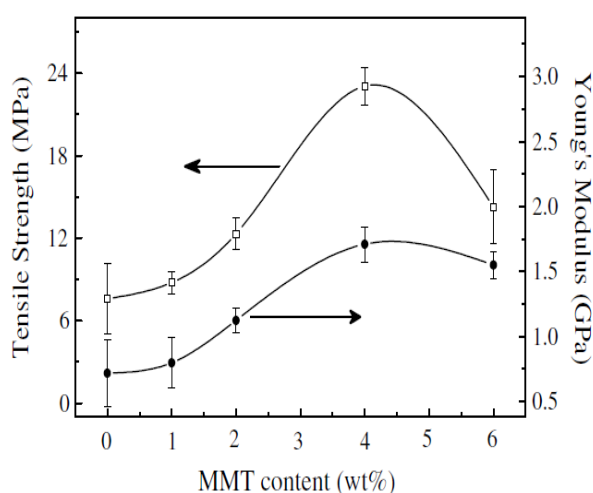

Fig. 8: Mechanical properties of PPC and PPC/OMMT nanocomposites with different OMMT contents (Shi & Gan, 2007).

Table 6: Mechanical Properties of PPC and PPC/VMT nanocomposites with different organo-vermiculite (VMT) content (Xu et al., 2005).

Composites	Yield strength, MPa	Engineering Modulus, MPa
Pure PPC	39.93	1001.0
PPC/ 2% VMT	37.57	1184.0
PPC/ 4% VMT	40.23	927.0
PPC/ 6% VMT	28.92	671.7
PPC/ 8% VMT	23.30	611.4

due to the large formation of silicate aggregates. These aggerates will act as stress concentration to reduce the mechanical properties of nanocomposites, which was displayed in Table 6. From this table, addition of nanoclay such as the organo-vermiculite (VMT), above 4% VMT, the nanocomposite shows decrease in the yield strength and elastic modulus as compared with the pure PPC.

6.0 Conclusion

Aliphatic polycarbonates are interesting polymer as it made up from carbon dioxide and epoxide. These polymers have weakness in term of mechanical and thermal properties due to the the flexible carbonate groups in backbone chains. This condition has limited the application of these aliphatic polycarbonates. However, the small amount of the nanoclay to these aliphatic polycarbonates show improvement in term of the flexibility, thermal and mechanical properties of the nanocomposites. The nano-scale dispersion of the nanoclay into these polymer matrices led to the improvement of these specified properties.

These studies more focused on the poly(propylene carbonate)/clay nanocomposites thermal and mechanical properties. Further investigation in term of applications wise which could help to increase the usage of this interesting nanocomposites for the oxygen and water barrier film is suggested to be carried out. Thus, modification of PPC with nanoclay acts as an alternative approach in mitigating the problems raised by the conventional polymer such as propylene and polyethylene. Besides, other type of these interesting aliphatic polycarbonates such as poly(ethylene carbonate) (PEC) with addition of nanoclay are noteworthy to be further carried out. Recently, PEC is tremendously studied by many researchers for the solid polymer electrolyte (SPE) development work. The research to improve the moisture absorption for this material is highly demanded and addition of nanoclay to PEC is suggested being an option to improve the moisture barrier of PEC film.

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