THERMAL DECOMPOSITION PROPERTIES OF RECYCLED TIRE RUBBER FILLED WOOD/HIGH DENSITY POLYETHYLENE COMPOSITES

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ABSTRACT

Dynamic thermo-gravimetric analysis under nitrogen was applied to investigate the thermal decomposition process of wood/HDPE composites (WPC) modified with different amount of ground tire rubber (GTR). Degradation models, including the Friedman and Flynn-Wall-Ozawa (F-W-O) were used to determine the apparent activation energy (Ea) of various materials. Composites with various GTR contents exhibited a similar two-stage degradation process. Initial decomposition temperature (T_0) of the composites gradually decreased from 250.1°C to 238.2°C with the increasing GTR concentration, while the peak temperature (T_p) values remained about the same. Kinetic analysis demonstrated an average activation energy decreasing with the incorporation of 5 % GTR within the composites through both methods, but no big difference was observed with further increasing the GTR content from 5 % to 15 %. The established thermal decomposition kinetic parameters allow developing the reutilization of waste tire rubber in composite materials with appropriate loading level.

KEYWORDS: Recycled tire rubber, wood plastic composite, thermo-gravimetric analysis, thermal decomposition kinetics, apparent activation energy.

INTRODUCTION

Environmental pollution from industrial wastes and waste living materials is always one of the biggest problems (Yang et al. 2004). Among these waste materials, ground tires are of

great concern due to the rapid development of automotive industry, resulting in a great demand of ground tires. In 2013, the total rubber consumption of China is more than 8.3 million tons, accounting for a third of the global rubber consumption. At present, the recycling rate of used tires is only about 65%, and there are nearly 950,000t non-biodegradable waste rubber, leading to the "black pollution". One promising recycling approach is to add waste rubber into natural fiber reinforced polymer composites. It is well known that natural fiber reinforced polymer composites possess the advantages of lower raw material costs and environmental issues as well as accredited mechanical properties. However, incorporation of natural fibers to polymer matrix will lead to significant decline in its impact strength, which seriously limits the practical application of the composites. Toughening agents were used to improve this situation, and elastomers such as ethylene propylene diene monomer (EPDM), natural rubber (NR), styrene butadiene rubber (SBR) and waste tire rubber were proved to be effective in increasing the impact strength. For example, Hristov (Hristov et al. 2004) investigated impact fracture behavior of polypropylene (PP)/wood fiber composites modified with maleated polypropylene as compatibilizer and poly (butadiene styrene) rubber as impact modifier. It was found that the elastomer impact modifier toughen the PP matrix and enhance the total fracture energy of the modified composites, also, an elastic to elastic-plastic transition fracture behavior was observed in the modified composites. Ruksakulpiwat (Ruksakulpiwat et al. 2009) used various contents of NR and EPDM as impact modifier in PP/vetiver grass composites. It was concluded that the impact strength and elongation at break were significantly increased with adding more than 20% NR or EPDM by weight and the composites with EPDM rubber showed slightly higher tensile strength and impact strength than that with NR.

According to previous research, natural fibers, plastomer and rubber can be combined in two ways. One is to use natural fibers to reinforce the thermoplastic elastomer (TPE) to obtain a blend of nature rubber and polyolefin. For this type of composites, previous research mainly focused on the effect of processing, the type of coupling agents, the types and loading levels of fibers, the types of rubber and various chemical treatments on the mechanical properties, morphologies, interfacial features and thermal stability (Khalf and Ward 2010, Anuar and Zuraida 2011, Abdelmouleh et al. 2007, Shubhra et al. 2010, Viet et al. 2012, Sonnier et al. 2008, Sliwa et al. 2012a, Sliwa et al. 2012b). The other method is the extrusion of these three materials through a direct mixing mode, which is not that rigorous as the first way in selecting raw materials, that is, the rubber can be natural or synthetic, single component or multicomponent, virgin or recovered.

The utilization of vulcanized or formulated recycled tire rubber will further reduce the raw material costs and "black pollution". This reutilization of rubber as additives to wood and the corresponding polymer materials have been explored with GTR in recent years (Yang et al. 2004, Zhao et al. 2008, Ramezani Kakroodi et al. 2013). Compared with pure WPC, a substantial improvement of impact strength and ductility with a slight decreasing in some other mechanical properties of the composites can be achieved. However, little is known about the effect of GTR content on thermal kinetics properties of the composites, which primarily determines the possibility of the application of waste tire rubber in composite materials (Sułkowski et al. 2006, Makarucha et al. 2001).

Kinetic determination of complex composites involves the knowledge of the reaction mechanisms. But the number of reactions that occur simultaneously in the degradation processes can be quite huge, which makes it practically impossible to develop a kinetic model that can apply in all cases. Therefore, classical kinetic analysis methods including Friedman and F-W-O were still useful in evaluating the kinetic properties of composite materials (Avella et al. 2010, Li et al. 2013, Yao et al. 2008). And in this work, GTR was introduced as elastic fillers into wood

flour (WF)/high density polyethylene (HDPE) composites. The objective of this research was to investigate the effect of rubber content on thermal stability of the HDPE-based composites. Thermal decomposition processes of the composites were evaluated through dynamic thermogravimetric analysis, while kinetic parameter of apparent activation energy Ea was determined by the two "model-free" methods mentioned above. We simply attempt to get a thoroughly fundamental understanding of our newly-produced composite materials.

MATERIAL AND METHODS

Theoretical basis

The fundamental rate equation applied in all kinetic studies is generally described as:

$$d\alpha/dt = kf(\alpha) \tag{1}$$

Where k is the rate constant; α is the conversion rate and f(α) is the reaction model, a function depending on the actual reaction mechanism. In this study, the conversion rate α is defined as:

$$\alpha = kf(W_0 - W_t)/(W_0 - W_f) \tag{2}$$

Where W_t, W_0 and W_f are time t, initial and final weights of the sample, respectively. The rate constant k is generally given by the Arrhenius equation:

$$k = A\exp(-E_a/RT) \tag{3}$$

Where Ea is the apparent activation energy (kJ·mol^{-1}); R is the gas constant (8.314J/k mol); A is the pre-exponential factor (min^{-1}); T is the absolute temperature (K). The combination of Eqs. 1 and 3 gives the following relationship:

$$d\alpha/dt = A\exp(-E_a/RT)f(\alpha) \tag{4}$$

For a dynamic TGA process, introducing the heating rate β (β=dT/dt) into Eq. 4, then Eq. 5 is obtained as:

$$d\alpha/dt = (A/\beta)\exp(-E_a/RT)f(\alpha) \tag{5}$$

Eqs. 4 and 5 are the fundamental expressions of analytical methods to calculate kinetic parameters with the TGA data.

The "model free" method used in this work, including Friedman and F-W-O methods, is listed in Tab. 1. The former directly leads to ($-E_a/R$) for a given value of α by plotting the term ln(dα/dt) against 1/T (Friedman 1964), while the F-W-O method leads to ($-E_a/R$) from the slop of the line determined by plotting logβ against 1/T at any certain conversion rate (Ozawa 1965, Flynn and Wall 1966).

Tab. 1: Kinetic methods for the evaluation of activation energy.

Method	Equation	Plots
Friedman	ln(dα/dt)=ln[A f(α)]-E_a/RT	ln(βdα/dT) against 1/T
F-W-O	logβ=log(AE_a/R f(α))-2.315-0.4567E_a/RT	logβ against 1/T

Raw material preparation

GTR, with particle size between 100 to 180 μm was obtained from a local garage. WF of southern pine from U.S.A with a size distribution between 150 to 180 μm was applied in this study. HDPE AD60-007 with MFR=0.7 g·10^{-1} min at 190°C/2.16 kg, density 0.96 g·cm^{-3} was provided by Exxon Mobile Chemical Co. (Houston, TX, USA). Maleic

anhydride-grafted polyethylene (MAPE EpoleneTM G2608 with MFR 6 to 10 g·10^{-1} min at 190°C/2.16 kg, MF=65.000 g·mol^{-1}, acid number 8 mg KOH·g^{-1}) from Eastman Chemical Co. (Kingsport, TN, USA). Polyethylene wax (PW H-108 with viscosity 4 to 200 mPas, molecular weightn 2000, melting point 105-110°C) was used as lubricant.

Compounding

All the raw materials were fed into a counter-rotating twin-screw extruder (Brabender Instruments Inc., Hackensack, USA) with a screw speed of 30 rpm. The blending ratios of the composites are listed in table 2. The mass ratio of WF to HDPE was fixed as 3/7, all other recipes were added based on the total mass of WF and HDPE, the adding levels for GTR were 0, 5%, 10% and 15%, for MAPE and PA, the figures were 2% and 1%, respectively. Processing temperature of the barrels was 150 (feeding zone)-175-175-175-175°C (die). The compounds were subsequently cooled in a cold water bath and then pelletized into granules at the die exit.

TGA procedures

A TG209F3Tarsus thermo-gravimetric analyzer (Netzsch Co. Selb, Germany) was used to test the thermal decomposition behavior of the composites. The temperature increased from room temperature to 700°C at five different heating rates of 5, 10, 20, 30, 40 K/min. The samples were dried in an oven at 60°C for 24h and were evenly distributed in a crucible with an initial sample amount of 5 mg (The sampling segment was set as 1s per point). The tests were performed in a high purity nitrogen (99.5% nitrogen and 0.5% oxygen) atmosphere under atmospheric pressure. Before each test, the furnace was purified by nitrogen steam for at least 20 min to guarantee an oxygen-free inert environment.

The TG and DTG curves were smoothed by adjacent averaging (number of adjacent points=8) method and analyzed using Proteus Analysis software from NETZSCH Instrument. Activation energy values were calculated with a specially designed program in MS Excel, and all graphs were created by Origin Pro 8.0.

Tab. 2: Blending ratio of the composite materials.

Sample	HDPE (wt.%)	WF (wt.%)	MAPE (wt.%)	PW (wt.%)	GTR (wt.%)
WPC	70	30	2	1	0
WPC/GTR-5	70	30	2	1	5
WPC/GTR-10	70	30	2	1	10
WPC/GTR-15	70	30	2	1	15

RESULTS AND DISCUSSION

Overall thermal decomposition processes of the materials

Fig. 1a shows the overall thermo-gravimetric decomposition processes of the main three raw materials (i.e., HDPE, GTR and WF) at a heating rate of 40 K·min^{-1} as an example. The main weight loss of WF occurred between 230~400°C, a distinct peak and an indistinctive shoulder peak were observed in DTG curve, corresponding to the decomposition of cellulose and hemicellulose, respectively. For GTR, two main peaks were notable in DTG curve, at about 405°C and 467°C, which was caused by the simultaneous degradation of the main components of the tire, principally NR, SBR and butadiene rubber (BR) (Williams and Besler 1995, Galvagno

et al. 2007). Due to the random chain scission occurring through a radical mechanism (Avella et al. 2010), HDPE showed a single mass loss process with a distinct peak in the DTG curve.

Decomposition processes of the composite materials at a heating rate of 40 K·min^{-1} are shown in Fig. 1b. All the composite materials exhibited a similar decomposition process: two mass loss stages were observed, and the degradation peaks of GTR were overlapped with the main peaks of WF and HDPE, resulting in an enhancement of the first weightlessness peak and a reduction of the second one.
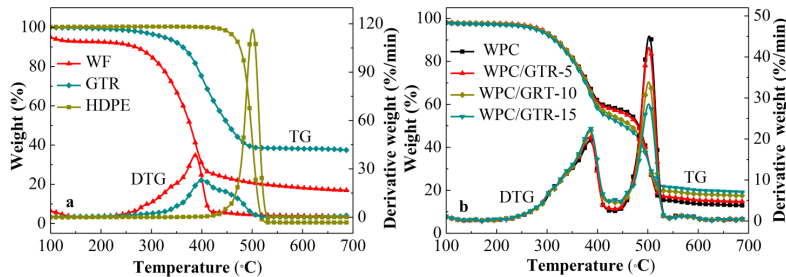

Fig.1: Thermal decomposition curves of the materials at heating rate of 40K/min (a–three raw materials; b–composite materials).

Thermal decomposition characteristics of the materials

The decomposition characteristics of the materials under various heating rates are summarized in Tab. 3. The initial temperature T_0, is assumed to corresponding to a solid mass loss fraction equal to 2.5%. The parameter T_p represents the peak temperature corresponding to the maximum decomposition rate obtained in DTG curve.

For all selected materials, the characteristic temperature points (T_0 and T_p) moved to a higher value with increasing in heating rate (Tab. 3), also, took WPC/GTR-10 as an example, the main degradation zone widened (Fig. 2), which were consistent with the findings of Sun (Sun et al. 2002). To avoid the influence of the heating rate, $T_{0\ \beta\rightarrow0}$ and $T_{p\ \beta\rightarrow0}$ were obtained by extrapolating β to where β=0 K·min^{-1} with each five values from the five heating rates (Fig. 3a). The obtained decomposition characteristics are listed in Tab. 4. There is no significant difference between WPC and WPC/GTRs in peak temperature, the initial temperature of WPC/GTRs moved to lower values compared with that of WPC. However, no big differences were found within WPC/GTRs, indicating a promising hint of the possibility in increasing rubber dosage in the composites without damaging thermal stability. Char yield of WPC/GTRs increased with the increasing adding amount of GTR, and the value for WPC/GTR-15 increased by 43% compared with pure WPC, indicating a potential role of the GTR in improving the thermal stability of the composites.

Tab. 3: Pyrolysis parameters of the raw materials.

| Sample	β (K·min⁻¹)	T_0 (°C)	T_p (°C)	Residue (%)
GTR	5	244.2	364.7	37.6
	10	246.5	378.3	36.9
	20	273.3	390.2	35.9
	30	276.6	397.5	37.6
	40	285.0	401.1	37.3
WF	5	229.5	334.7	17.6
	10	234.5	361.0	17.0
	20	241.7	372.5	17.1
	30	250.2	379.9	18.2
	40	243.9	387.3	16.8
HDPE	5	411.3	470.5	1.0
	10	409.4	471.7	0.5
	20	437.8	490.5	0.5
	30	444.5	496.2	0.1
	40	451.2	501.2	0.5
WPC	5	251.3	466.9	13.2
	10	255.3	476.1	10.3
	20	275.1	489.5	15.1
	30	271.8	497.3	13.4
	40	278.7	502.5	12.9
WPC/GTR-5	5	246.2	467.2	16.1
	10	252.3	478.2	14.1
	20	269.1	490.1	17.0
	30	272.0	498.3	14.9
	40	280.1	502.7	14.6
WPC/GTR-10	5	244.7	463.3	18.2
	10	244.0	475.7	14.3
	20	269.9	490.5	18.7
	30	274.4	497.9	16.5
	40	276.3	502.1	17.4
WPC/GTR-15	5	241.7	467.2	19.9
	10	245.1	475.4	15.8
	20	265.1	490.1	19.2
	30	271.8	496.3	19.2
	40	274.9	503.1	19.1
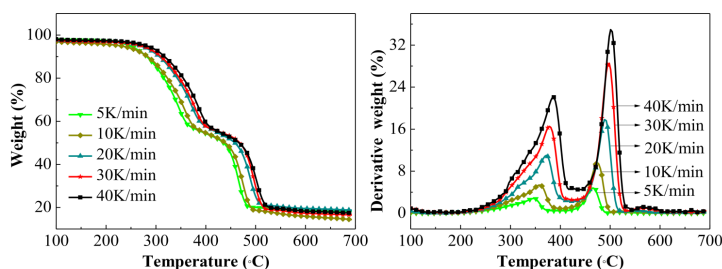
Fig. 2: TG and DTG curves of the WPC/GTR–10 at different heating rate.

Tab. 4: Decomposition parameters of the materials (β→0).

Samples	$T_{0\,\beta\to0}$ (°C)	$T_{p\,\beta\to0}$ (°C)	$Wp^{a}_{\beta\to0}$ (%)	Residue [b] (%)
WF	229.7	339.4	34.1(5.5)	17.4(0.6)
GTR	238.7	365.5	16.4(5.9)	37.1(0.7)
HDPE	403.9	466.1	28.0(26.9)	0.3(0.5)
WPC	250.1	465.3	52.6(9.1)	13.0(1.7)
WPC/GTR-5	243.8	466.5	53.4(8.7)	15.3(1.2)
WPC/GTR-10	240.0	463.2	54.7(7.0)	17.1(1.7)
WPC/GTR-15	238.2	465.1	56.7(6.6)	18.6(1.6)

[a] Weight loss corresponding to $T_{p\,\beta\to0}$; [b] Mean value from five heating rates; Numbers in parenthesis denote standard deviations.

Thermal decomposition kinetics

In order to further understand the decomposition properties of the composites and the influence of GTR on these properties, apparent activation energy *Ea* was calculated through the Friedman and F-W-O methods. The conversion rate range was α=0.1-0.9, with steps of 0.1. The Friedman plots for WF, GTR and WPC/GTR-5 are shown in Fig. 3b, 3c, and 3d as the example, and Fig. 3e, 3f shows the Ea of WPC and WPC/GTR-10 calculated by F-W-O method. In Figure 3b, the fitted lines of different conversion rates from 0.2 to 0.8 were nearly parallel, the differences occurred at α = 0.1 and α = 0.9 were probably due to the moisture and ash content existed in WF, which resulted in a complex decomposition during the starting and ending periods. Consequently, selected conversion rates of α = 0.2-0.8 were applied in calculating the *Ea* values. For GTR, the Friedman plots were approximately parallel except that at low conversion rate (α=0.1), indicating that the degradation process could be described as first order reaction, which was consistent with the literature results (Conesa et al. 1997). This first order reaction of GTR was the result of the independence of each fraction in the decomposition process. Lin studied the degradation characteristics of SBR, BR and their mixture, showing that the co-pyrolysis of these two kinds of rubber was independent on one another (Lin et al. 1998). The slop of the fitted curve at α = 0.1 was distinguished from the other ones, which was probably caused by the complex reactions of the small amounts of additives in GTR. Disparity in the fitted curves at low conversion rate compared with other groups was observed in WPC and WPC/GTRs as well (Fig. 3d, 3e and 3f).
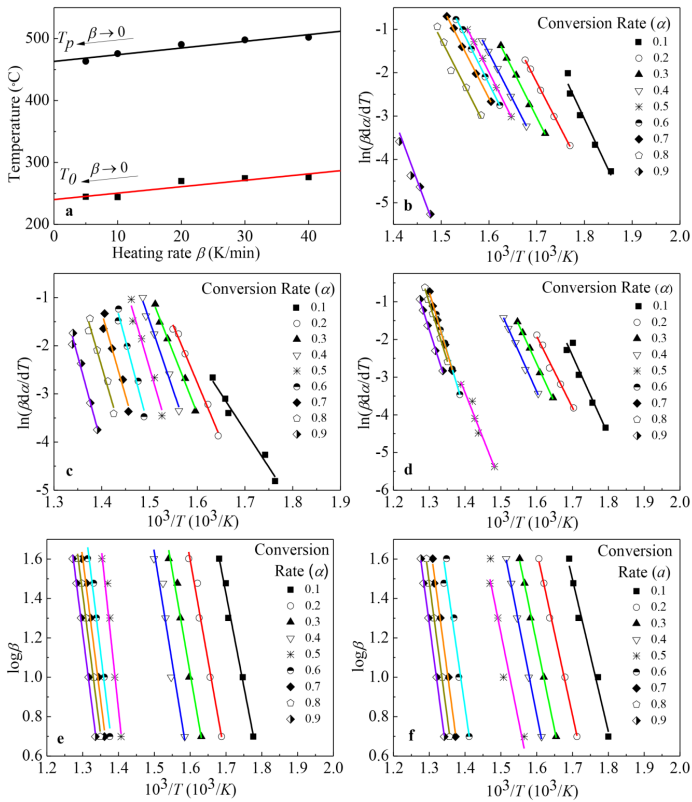
Fig. 3: (a) Determination of T_0 and T_p with WPC/GTR-10 as an example; (b–d) Determination of Ea by Friedman method (b–WF; c–GTR; d–WPC/GTR-5); (e–f) Determination of Ea by F-W-O method (e–WPC; f–WPC/GTR-10).

The Friedman plots of the composite materials (Fig. 3d) were somewhat different from that of Fig. 3b and 3c. Vertical coordinates of Friedman plots represent the differential of conversion rate (α) with respect to time (t). The value indirectly reflects the weight loss rate of the materials. Each component of the ternary composites had its own decomposition temperature range and weight loss rate. Consequently, in Fig. 3d, the fitted curves distributed into two regions, the first area (α = 0.1~0.4) mainly represented the weight loss process of WF and fractional GTR, while the second area (α = 0.5~0.9) predominantly demonstrated that of HDPE, which was proved to lose weight rapidly above 500°C (Kin et al. 2004), therefore, the fitted curves moved to higher value significantly. The fitted curve of α = 0.5 is a little different from others, the quite lower position indicated that, in this region, the weight loss process became fairly slow, probably caused by the decomposition of lignin and the rest of the tire rubber. This zoned phenomenon was observed in F-W-O method as well (Fig. 3e and 3f). Thus, it is necessary to take this into account when exploring the effect of rubber content on thermal properties of the composites and the activation energy marked as Ea_1, Ea_2 and Ea were introduced to represent the average activation energy of the first area, the second area and the whole process, respectively.

Tab. 5: Activation energy of the materials calculated by the two methods.

Sample	Friedman				Flynn-Wall-Ozawa			
	Ea_1 (kJ·mol^{-1})	Ea_2 (kJ·mol^{-1})	Ea (kJ·mol^{-1})	R^2	Ea_1 (kJ·mol^{-1})	Ea_2 (kJ·mol^{-1})	Ea (kJ·mol^{-1})	R^2
WF	-	-	180.2	0.9920	-	-	179.1	0.9990
GTR	-	-	280.3	0.9945	-	-	263.4	0.9957
HDPE	-	-	255.1	0.9960	-	-	242.7	0.9979
WPC	191.5	270.3	235.3	0.9943	181.5	265.0	227.9	0.9964
WPC/ GR-5	166.0	246.5	210.7	0.9979	163.7	240.8	206.6	0.9967
WPC/ GR-10	159.9	239.0	203.9	0.9873	157.1	237.3	201.7	0.9950
WPC/ GR-15	170.7	230.0	203.6	0.9986	166.3	229.6	201.5	0.9917

Ea_1, Ea_2, Ea and the correlation coefficient R^2 of the three raw materials and the composite materials are summarized in Tab. 5. Similar results were obtained through both methods, but the activation energy calculated by Friedman method is a little higher than that by F-W-O method for all selected materials. Ea values of the three raw materials differed from each other, with the highest value for GTR and the lowest for WF. For the composite materials, activation energy of the second area and the whole process decreased with the increasing amount of GTR. As to Ea_1, it firstly decreased with the increasing rubber content, but when the adding level reached 15%, the values increased from 159.9 kJ·mol^{-1} to 170.7 kJ·mol^{-1} (Friedman), and, 157.1 kJ·mol^{-1} to 166.3 kJ·mol^{-1} (F-W-O). The rising in Ea_1 value of WPC/GTR-15 is a promising hint for growing adding amount of rubber in the ternary composites.

Fig. 4 displayed the activation energy Ea calculated by Friedman and F-W-O methods of the three raw materials and the composite materials changed with conversion rates (α) in the entire pyrolysis process, respectively. In both methods, change of Ea values with conversion rate was basically the same. In Fig. 4a, Ea values of WF maintained around 180 kJ·mol^{-1}, according with the results of natural fibers in related literatures (Milosavljevic and Suuberg 1995, Nada and Hassan 2000, Varhegyi et al. 1989). Ea values of HDPE were about 250 kJ·mol^{-1}, and the values slightly changed with the increasing conversion rate. GTR had an Ea range varied from 120 kJ·mol^{-1} to 330 kJ·mol^{-1}, which was mainly caused by the complexity of its component such as NR, SBR and BR (Sułkowski et al. 2004). In addition, cracking reaction and cross-linking reaction may occurred during the decomposition process, leading to the variation in Ea values. The Ea range of GTR contained (or overlapped with) that of WF and HDPE, resulting in the changes of both Ea_1 and Ea_2 of WPC/GTRs in Tab. 5. In Fig. 4c, with the combination of GTR, Ea values of whichever conversion rate of WPC/GTRs were lower than that of WPC, and Ea value of α=0.5 of WPC was a little different from that of WPC/GTRs, a spurt was observed. The pyrolysis process of WPC was mainly divided into two stages, the first stage was the decomposition of cellulose and hemicellulose, with average Ea value approximately of 180 kJ·mol^{-1} (184.2 kJ·mol^{-1} for Friedman and 181.5 kJ·mol^{-1} for F-W-O). Degradation of HDPE mainly constituted the second stage, and Ea values increased rapidly in this period due to the low reaction activity of HDPE. Based on the mechanism of free radical chain reaction, the pyrolysis processes of vinyl polymers were just involved in the fracture of main chain, having nothing to do with the reaction of lateral groups. Therefore, the spurt in Ea value was the activation energy of its main chain scission, and the experiment values in present work were 312.6 kJ·mol^{-1}
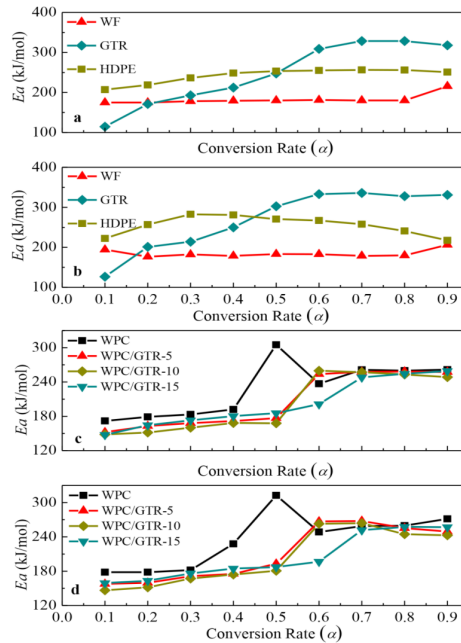
Fig.4: Changes of Ea values of raw materials and composite materials as a function of α by two methods (a, c– F-W-O method; b, d–Friedman method).

(Friedman) and 305.1 kJ·mol^{-1} (F-W-O), close to the literature result (326 kJ·mol^{-1}) (Marongiu et al. 2007). In WPC/GTRs, such activation energy value of α=0.5 was not observed, indicating that the amorphous rubber may have altered the crystallization and crystallinity of HDPE. In the melting process, rubber was unable to diffuse into the spherulitic growth sites, and it would be gripped by the crystalline region, thereby obstructing the spherulite growth rate and decreasing the polymerization degree (Jayasree and Predeep 2012), and then the new HDPE/rubber phase containing defective spherulite would exhibit lower mechanical strength and poorer thermal stability (Gao et al. 2010, Muniyandi et al. 2013). The lower *Ea* values of WPC/GTRs may, to some extent, be attributed to the weak interfacial interaction between the reinforcement phases (i.e., wood fibers, rubber crumbs) and the plastic matrix as well, since a favorable interface bonding would be beneficial for thermal properties(Avella et al. 2010).

CONCLUSIONS

Dynamic TG analysis was applied to investigate the thermal decomposition process of the composite materials fabricated by WF, GTR and HDPE. Flynn-Wall-Ozawa and Friedman methods were used in determining the apparent activation energy of the composites.

Composites with different rubber content exhibited a similar degradation process, all divided into two mass loss stages, mainly corresponding to the decomposition of cellulose/hemicellulose and high density polyethylene. The pyrolysis process of GTR overlapped with the two stages

due to the simultaneous degradation of the main components of the tire, principally NR, SBR and BR. Initial decomposition temperature T_0 slightly reduced from 250.1°C to 238.2°C with the increasing rubber concentration, while the peak temperature T_p values remained about the same within WPC and WPC/GTRs. Kinetic analysis demonstrated an average activation energy decreasing with the increasing rubber content through both methods, yet it was still promising for growing loading level of rubber in the composites, for the very close Ea values between WPC/GTRs and the ascending Ea_1 value observed in WPC/GTR-15.

ACKNOWLEDGMENT

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