

Degradation Kinetics of Poly(HDDA-co-MMA)

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ABSTRACT: 1,6-hexanediol diacrylate (HDDA) and methyl methacrylate (MMA) were copolymerized in different weight ratios using UV light induced photo-polymerization to give poly(HDDA-co-MMA). Differential scanning calorimetry shows that copolymer was formed. The thermogravimetric and differential scanning calorimetric studies with different heating rates were carried out on these copolymers to understand the nature of degradation and to determine its kinetics. Different kinetic models were

adopted to evaluate various parameters like the activation energy, the order, and the frequency factor. These analyses are important to study the binder removal from 3D-shaped ceramic objects made by techniques like Solid free form fabrication. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2444–2453, 2010

Key words: thermogravimetric analysis; pyrolysis; glass transition; differential scanning calorimetry

INTRODUCTION

Solid free form fabrication (SFF) is one of the emerging technologies to obtain complex three-dimensional objects from CAD design.^{1,2} Several SFF techniques have already been commercialized through which it is possible to fabricate net shape prototypes in a short time. Stereo-lithography is a popular technique to form the designed structure in a layered manner. In this technique, a liquid monomer with an appropriate photo-initiator is polymerized by moving a high-energy laser beam according to the 3D CAD data.

In the last decade, there have been efforts to miniaturize the process to realize the structures in micron regime. In this process, the focused laser spot is kept fixed and the build platform moves in the X–Y direction. In this technique, the critical issue that should be addressed in achieving the structure in micron size is the high-surface tension that results due to the enhancement of surface to volume ratio as the size is reduced. To overcome this problem, a low viscous monomer is chosen.³ 1,6-hexanediol diacrylate (HDDA) is a well-known monomer which has been extensively exploited due to its low viscosity.^{4,5} To fabricate a ceramic object by this technique, ceramic particles have been blended with desired monomer with an appropriate plasticizer and dispersant. With the application of laser, photo-poly-

merization of the monomer takes place, which acts as a binder in the system. The kinetics of photo-induced process plays an important role in controlling the polymerization.

The kinetics of photo-polymerization of HDDA and along with Al₂O₃ ceramic have been studied extensively by differential photo calorimetry (DPC).^{6–8} After realizing the net shape, it is equally important to eliminate the organic content without shape deformation. The uncontrolled removal of polymers during binder burn-out process can lead to micro cracks and weakening of shapes. Therefore, it becomes crucial to understand the nature of degradation kinetics. The binder removal studies using PMMA as binder with alumina ceramic has been investigated in our earlier work.⁹ To the best of our knowledge, there is no report on the mechanism of degradation kinetics of PHDDA and its copolymer with PMMA.

Thermogravimetry is widely used to characterize the decomposition mechanism of many polymeric materials. Depending on the experimental conditions (nonisothermal, isothermal) during thermogravimetric analysis (TGA), several methods have been developed like Friedman, Chang, Kissinger, Flynn, Flynn-Wall, Freeman-Carrol, Chatterjee-Conrad, and Horowitz-Metzger.^{10–12} In this report PHDDA and PMMA are copolymerized with different weight fraction and studied by using different models of thermal analysis. The various techniques such as Kissinger, Ozawa, Friedman, Chang, and Flynn were applied to model the kinetics of degradation process. A detailed kinetic study has been carried out to predict the effect of PMMA addition on the degradation and thermal stability of PHDDA using isothermal and nonisothermal thermogravimetric data.

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EXPERIMENTAL

1,6-HDDA monomer (80%) and benzoin ethyl ether (BEE) photo-initiator were obtained from Sigma Aldrich, Germany and Sigma Aldrich, USA respectively. Mono-methyl methacrylate (99%) was supplied by Rolex Chemical, India. The purification of HDDA and MMA was carried out by washing with 5M NaOH solution (maintaining a (1 : 3) volume ratio of monomer to caustic soda) followed by washing with deionized water, to make the monomers free from inhibitor.⁶ The monomers were dried over MgSO₄ and stored in dark at 0°C. The composition of MMA in HDDA monomer is varied from 0 to 75 as a weight percent with a step of 25% interval. The codes given to the sample are PHDDA, Phpm7525, Phpm5050, Phpm2575 and PMMA, respectively. Photo-initiator (1 wt %) was mixed with all the compositions of monomer at 25°C. The mixtures were kept in a photo-chemical reactor for 30 min for bulk polymerization to obtain the copolymer. The photo-chemical reactor used in this study consisted of a jacketed quartz tube of 3.4 cm inner diameter, 4 cm outer diameter, and 20 cm length. A high pressure 125-W mercury vapor lamp (Phillips, India) was placed inside the reactor. Cold water was circulated through the jacketed quartz tube to keep the temperature of the surrounding not beyond 40°C. The lamp radiates predominantly at 365 nm (3.4 eV). The photon flux of the lamp measured by UV light meter probe (Digital Instruments) was 40 W m⁻². The semisolid polymers resulting after the polymerization reaction was kept in the hot plate at 60°C for 10 h to remove the unconverted monomer and oligomers. The degradation of copolymer compositions was studied by pyrolysis.

The thermogravimetric measurements were carried out by TA instruments SDT Q600. TG/DTA experiments have been done for PHDDA samples in N₂ gas flow with varying heating rates 2, 5, 10, 15, 18, and 20 K/min and the same samples were pyrolyzed at 10 K/min heating rate in ambient atmosphere. TGA of PHDDA and PMMA blends were carried out at 10 K/min heating rate in N₂ atmosphere. The sample weight for the measurement was taken around 10 ± 2 mg. The isothermal TG analyses were performed from 350 to 400°C at 10°C intervals. In all cases the flow rate of the gas was kept 100 mL/min.

The conventional differential scanning calorimetry (DSC) and modulated DSC (MDSC) experiments have been carried out using TA Q200 instrument. The samples were equilibrated at -50°C and heated to 200°C at 10 K/min heating rate for the purpose of measurement by conventional DSC. The gas flow rate of N₂ was kept at 50 mL/min. MDSC experiments have been performed at a modulation of ±1 K/min for every 80 s followed by 300 s isothermal

and at heating rate of 2 K/min. Liquid nitrogen was used to keep the flange temperature at -175°C of the DSC cell. The heat-cool-heat cycle was repeated for all the runs of MDSC. In all the experiments, hermetic-sealed aluminum pans have been used. The kinetics of thermal degradation process has been studied using various techniques discussed below.

MODELS FOR PYROLYSIS

Dynamic and isothermal thermogravimetric analyzes are extensively used to determine the kinetic parameters of degradation of polymers by thermally activated process. The degradation rate is as follows:

$$\frac{d\alpha}{dt} = Zf(\alpha) \exp(-E_a/RT) \quad (1)$$

where α is the fractional weight loss or conversion at any time t , $f(\alpha)$ represents some function of this conversion. α can be evaluated from the following relation,

$$\alpha = \frac{(M_0 - M_t)}{(M_0 - M_f)} \quad (2)$$

where M_0 and M_f are initial and final weight of the sample and M_t is the sample weight at any time t . Z and E_a represents the pre-exponential factor and apparent activation energy, respectively. R is the universal gas constant and T represents the sample temperature in Kelvin at any time t . The thermogravimetric data obtained by pyrolysis have been analyzed by following techniques, which are based on single and multiple heating rates, and are discussed in the following section.

Single heating rate

Friedman technique

Friedman technique¹³ is used on the basis of single heating rate data of TGA. This method is based on comparison of mass loss rates ($d\alpha/dt$) for a fractional mass loss α . The natural logarithm of eq. (1) on both sides gives the following,

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln Z + \ln f(\alpha) - \frac{E_a}{RT} \quad (3)$$

where $f(\alpha)$ is the function of conversion and is represented as follows,

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

The apparent activation energy is calculated from the slope of the linear plot $\ln(d\alpha/dt)$ vs. $1/T$ for constant α . In addition, the slope of $\ln f(\alpha)$ vs.

$1/T$ provides order of the reaction (n). Frequency factor of collision, Z , can be evaluated from the intercept of the equation.

Chang technique

Chang method¹⁴ is also used to calculate the various kinetic parameters from single heating rate thermogram. Rearranging eq. (1) and assuming the kinetics as a decomposition reaction, the following equation can be obtained.

$$\ln \left[\frac{(d\alpha/dt)}{(1-\alpha)^n} \right] = -\frac{E_a}{RT} + \ln Z \quad (5)$$

Hence the plot of $\ln \left[\frac{(d\alpha/dt)}{(1-\alpha)^n} \right]$ vs. $1/T$ can be used to obtain the activation energy, order and frequency factor Z .

Multiple heating rate

Kissinger technique

The principle of Kissinger technique¹⁵ is to use variable heating rate to calculate apparent activation energy, order and collision time of a decomposition reaction by thermally activated process. It calculates the activation energy at maximum decomposition rate of reaction at different heating rates. Differentiating eq. (1) and setting it to zero yields,

$$\frac{E_a q}{RT_{dm}^2} f(\alpha) = f'(\alpha)_m \left(\frac{d\alpha}{dt_m} \right) \quad (6)$$

where $q = dT/dt$ (heating rate) and T_{dm} = decomposition temperature at maximum weight-loss rate, which is the highest point of the differential thermogravimetric curve.

$$\left(\frac{E_a q}{RT_{dm}^2} \right) f(\alpha) = f'(\alpha)_m Z f(\alpha)_m \exp \left(-\frac{E_a}{RT_{dm}^2} \right) \quad (7)$$

Rearranging eq. (4) results in the following,

$$\frac{d \left[\ln \left(\frac{q}{T_{dm}^2} \right) \right]}{d \left(\frac{1}{T_{dm}^2} \right)} = -E_a/R \quad (8)$$

Hence, eq. (5) can be used to determine the activation energy, the order and collision factor of the degradation reaction by pyrolysis.

Ozawa technique

Ozawa method¹⁶ is derived by integrating and rearranging the eq. (1) which gives,

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{Z}{q} \int_{T_0}^T \exp \left(-\frac{E_a}{RT} \right) dT \quad (9)$$

where q is heating rate dT/dt and Z is frequency factor. Doyle's approximation¹⁷ transforms the above equation as follows:

$$\log \left[\int_0^\alpha \frac{d\alpha}{f(\alpha)} \right] = \log \left(\frac{ZE_a}{R} \right) - \log q - 2.315 - 0.4567 \left(\frac{E_a}{RT} \right) \quad (10)$$

The activation energy is obtained from the slope of the linear plot of $\log q$ vs. $1/T$ at fixed conversion for different heating rates. This method¹² represents a relatively simple method of determining activation energies directly from the plot of weight loss with temperature obtained at several heating rates. This technique assumes that Z , $(1-\alpha)$, n , and E_a are independent of T , whereas Z and E_a are independent of α .

Isothermal method

Flynn technique

The kinetic parameter can be evaluated, using the following Flynn equation¹⁸ which is based on the isothermal TGA data as follows,

$$\ln(t) = \ln[(1-2\alpha)/Z] + \frac{E_a}{RT} \quad (11)$$

For a certain weight loss α , the natural logarithm of time is linearly dependent to the inverse of the absolute temperature T . Assuming the order remains constant within that weight-loss interval and temperature, the slope of the plot provides the apparent activation energy. The frequency of collision, i.e., $\ln Z$ can be obtained from the intercept of the curve.

RESULTS AND DISCUSSIONS

DSC analysis

Since glass transition of the binder affects the rheological properties of ceramic polymer blend, it is crucial to know about T_g of the polymeric binder.¹⁹ DSC experiments have been carried out to determine the glass transition temperature (T_g) of PHDDA and the variation of glass transition with different concentrations of MMA in HDDA in copolymers. T_g has been determined from the temperature at the point of intersection between the tangents drawn at the point of inflection of the transition and at the flat part of the curve before the transition.²⁰ The glass

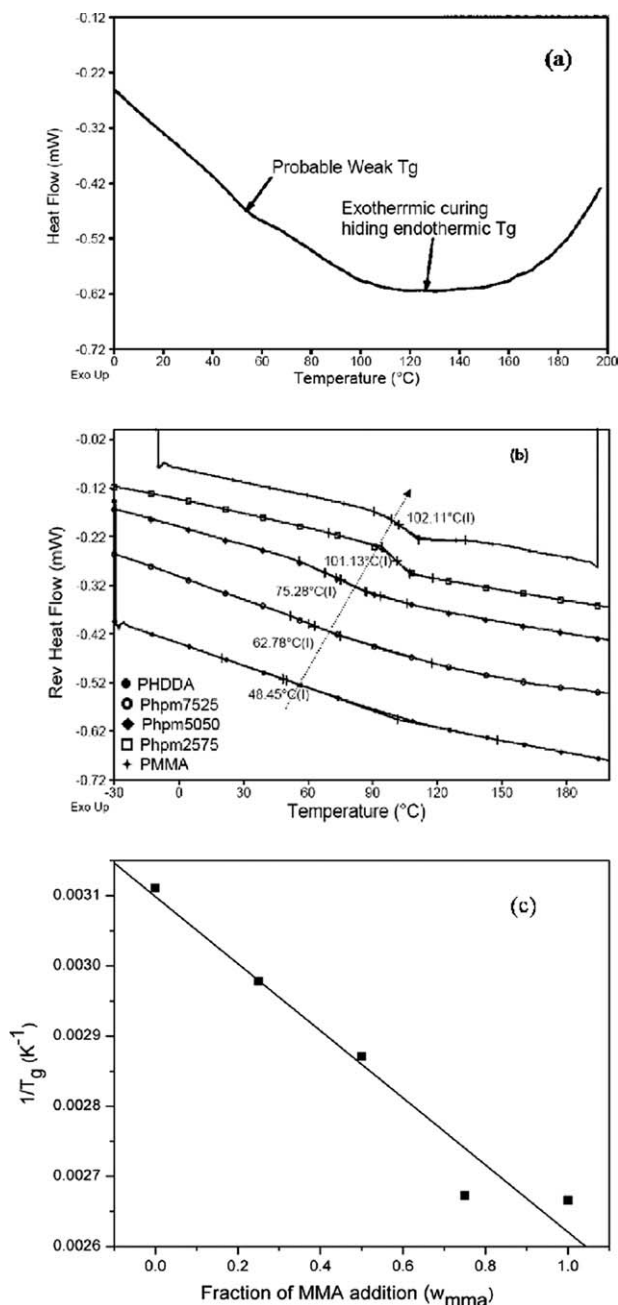


Figure 1 (a) Conventional DSC plot of PHDDA (b) Modulated DSC plots of poly (HDDA-co-MMA) copolymer of different compositions (c) Plot of Fox equation.

transition of PHDDA, however, could not be resolved by conventional DSC experiment. An exothermic curing as shown in Figure 1(a) precludes the appearance of endothermic T_g . Hence, modulated DSC (MDSC) was employed with an intention to determine T_g of the sample. In MDSC, the total heat flow of a system is divided into reversible and non-reversible heat flow and T_g is differentiated from the enthalpic relaxation.²¹ A very feeble change in heat flow signal has been noticed in the range of 35°C to 100°C in the reversible heat flow vs. temperature

curve shown in Figure 1(b), which indicates a very broad glass transition around 48°C. With the increment of MMA in HDDA system as a copolymer, the glass transition becomes prominent. A distinct glass transition at 102°C has been observed for PMMA as seen in Figure 1(b,c) which matches well with the reported value of T_g obtained for atactic PMMA.²² The reduction in the value of T_g from the parent PMMA composition may be due to penetration of bulky chain of PHDDA molecules between PMMA which disrupts the chain alignment and reduces the van der Waals bonding between the adjacent chains thereby providing more free volume in the system. The inverse of T_g data are observed to be linear with increasing mass fraction of MMA in the copolymer shown in Figure 1(c) which satisfies the Fox equation²³ described by the following:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (12)$$

where w_1 and w_2 are the weight fraction of each monomer in the copolymer and T_{g1} and T_{g2} are the absolute glass transition temperature of the respective homopolymers. Thereby, it is conclusive that PHDDA and PMMA form a copolymer in every composition.

TGA of PHDDA and the copolymer at different heating rate

TGA and corresponding differential thermogravimetry (DTG) curve of PHDDA with multiple heating rates from 2 to 20 K/min in N₂ atmosphere at the flow rate of 100 mL/min is shown in Figure 2(a,b), respectively. The comparative thermogravimetric study carried out for PHDDA, Phpm2575, Phpm5050, Phpm7525, and PMMA at 10 K/min under N₂ atmosphere is plotted in Figure 3. It is seen from the DTG curve that there is a single step weight loss during degradation process for both PHDDA and its copolymer with PMMA. Thermosetting polymers are covalently bonded three-dimensional networks which decompose to form volatile degraded product followed by charring when heated up to its decomposition temperature. PHDDA also degrades through random chain scission and chain end scission mechanism and results in carbon residue. The pyrolysis of PMMA is well discussed in literature.^{24,25} The multiple decomposition stages in PMMA are evident by multiple DTG maxima, which are shown in Figure 3(b). This can be attributed due to the depolymerization of PMMA, which is generally initiated by the scission of head-to-head bonds, at unsaturated chain ends, and by main chain scission producing trace amount of residue carbon. The β C-C scission is the reason of depropagation of

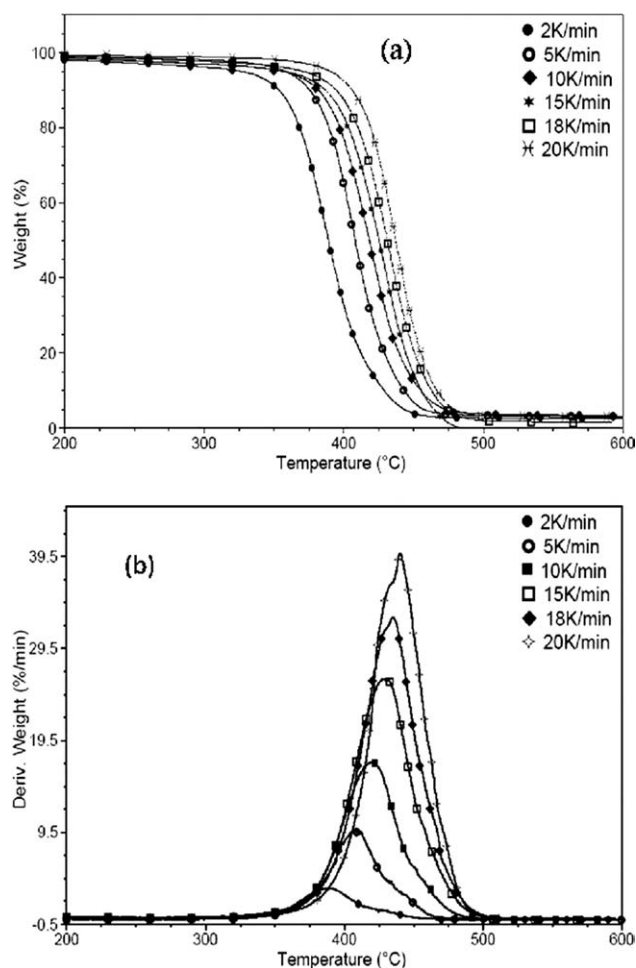


Figure 2 (a) TGA and (b) DTG curve of PHDDA at different heating rate.

radicals for PMMA.²⁶ The degradation of PMMA shows high to moderate activation energy depending on the molecular weight. The low activation energy of PMMA is observed due to its thermally labile end groups, which are formed during the bulk polymerization. Figure 3 shows the thermal stability decreases with the increasing content of PMMA in copolymer. The motivation of the study is to optimize the thermal stability and residual carbon in such kind of blends.

Kinetic study of PHDDA pyrolysis by Friedman and Chang techniques using single heating rate

The kinetics of thermal decomposition of a system by single heating rate thermogram data and inter-comparison of kinetics which were carried out at several heating rates can be properly explained by Friedman and Chang techniques. The kinetic studies were carried out on PHDDA and its copolymer with PMMA using these techniques. The decomposition process of PHDDA as a single system was studied with several heating rates (from 2 to 20 K/min). The

kinetic parameters were evaluated using eqs. (3) and (4). The Friedman plot of PHDDA for different heating rates has been plotted in Figure 4(a). A family of straight lines is obtained for the plots of $\ln(d\alpha/dt)$ vs. $1/T$ and $\ln(1 - \alpha)$ vs. $1/T$. Since these lines of

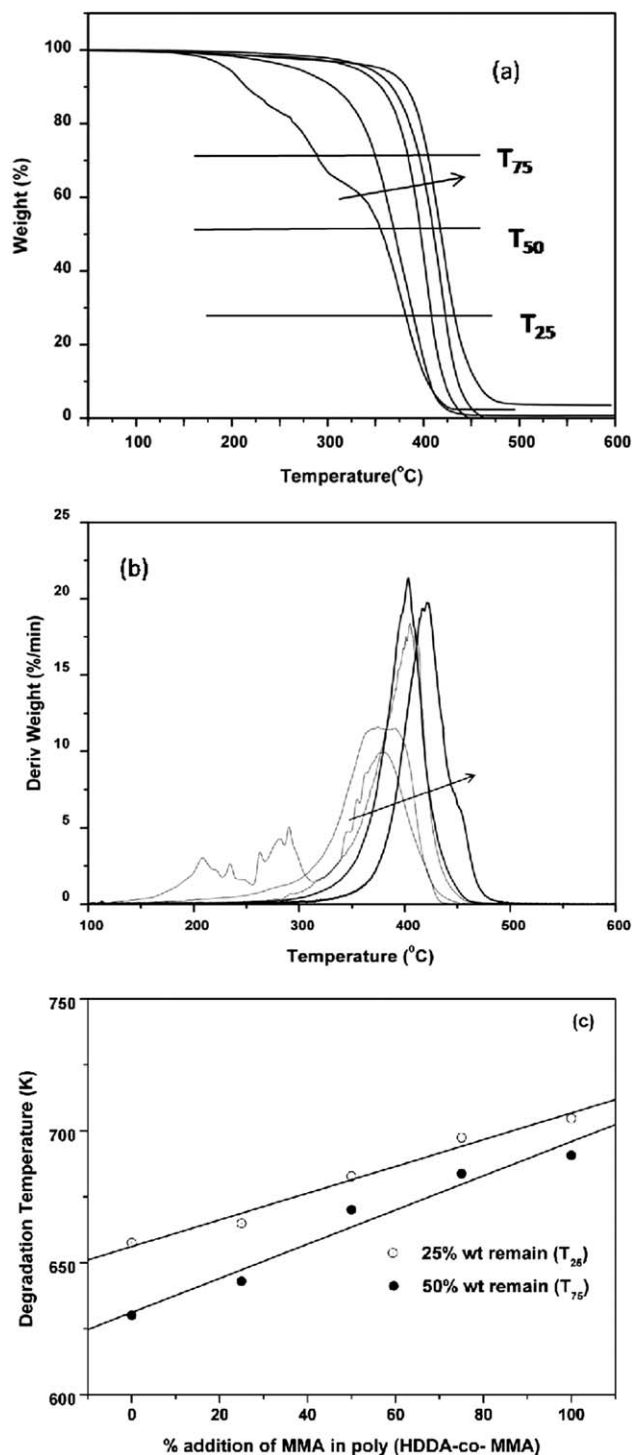


Figure 3 (a) TGA, (b) DTG curve of poly(HDDA-co-MMA) copolymer of different composition at 10°C/min. The direction of arrow indicates the decreasing MMA content in copolymer. (c) Plot of T_{25} and T_{50} with the function of MMA addition in poly(HDDA-co-MMA).

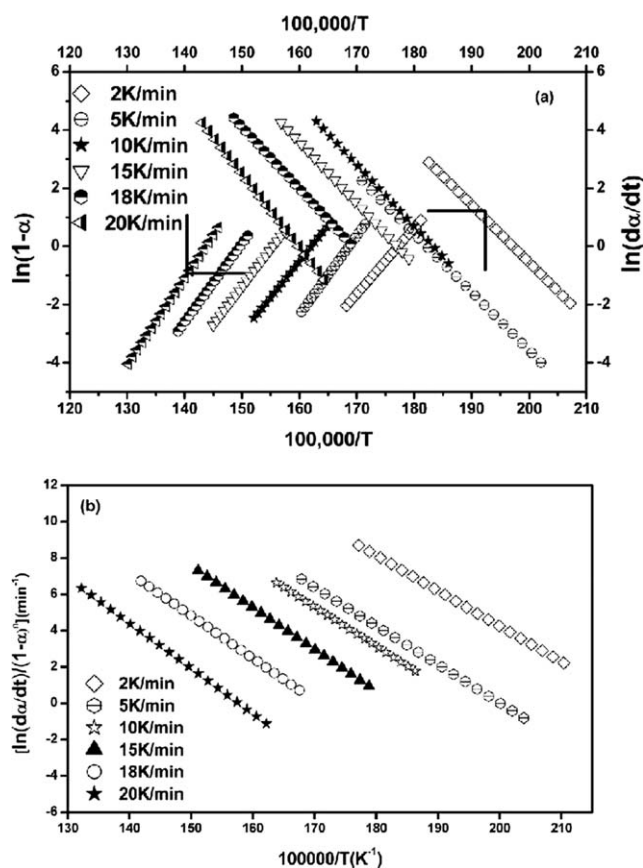


Figure 4 (a) Friedman Plot and (b) Chang Plot of PHDDA sample.

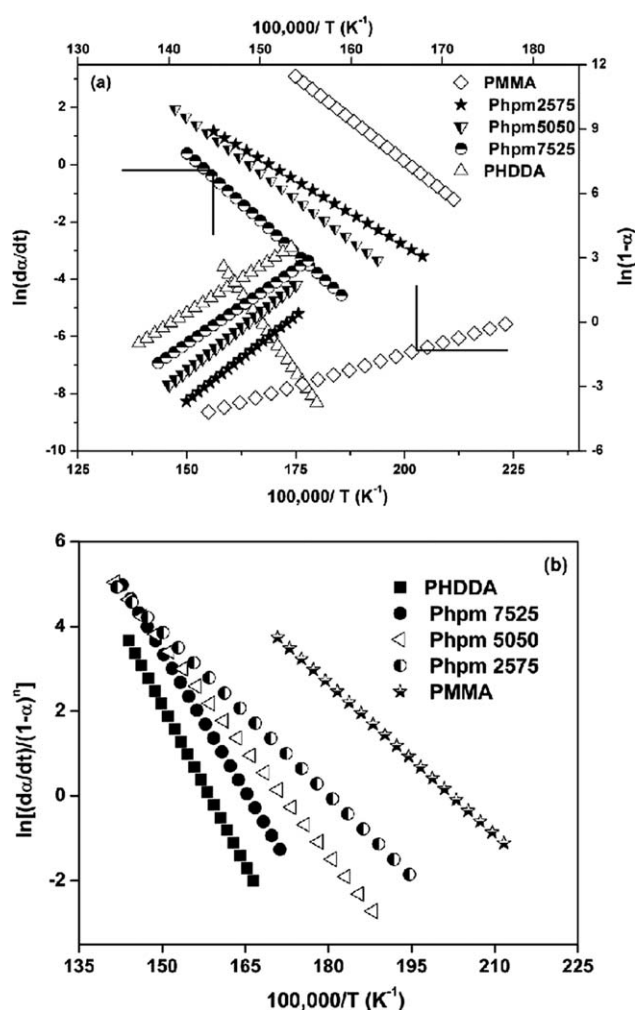


Figure 5 (a) Friedman Plot (b) Chang Plot of Poly (HDDA-co-MMA).

the plots overlapped on each other, the 2D waterfall Graph (in Origin version 7.5) with 60% offset has been used to represent the distinct and clear view. The set of straight lines showed the regression coefficient in the range 0.967–0.996. The kinetic parameters of PHDDA at different rates were calculated by the Chang technique using eq. (5). The set of lines for the plot between $(\ln(d\alpha/dt)/(1-\alpha)^n)$ vs. $1/T$ and is shown in Figure 5. The regression of all lines lies in the range 0.991–0.998. The kinetic parameters calculated from both the techniques are listed in Table I.

It is found that the apparent activation energy significantly increases with higher heating rates as has been evaluated by both the techniques. It is evident from Table I that activation energy increases steadily from 2 to 20 K/min. It has also been observed that order calculated from both the techniques is 0.9 for heating rates from 2 to 10 K/min and it decreases from 0.8 to 0.7 as the heating rates progress from

TABLE I
Kinetic Parameters of Thermal Decomposition of PHDDA at Different Heating Rate Using Friedman and Chang Technique

Heating rate (K/min)	Friedman			Chang		
	E_a (kJ/mol)	n	$\ln Z$ (min^{-1})	E_a (kJ/mol)	n	$\ln Z$ (min^{-1})
2	164	0.9	32	162	0.9	31
5	166	0.9	32	176	0.9	32
10	176	0.9	34	179	0.9	34
15	178	0.8	34	192	0.8	37
18	191	0.8	37	195	0.7	37
20	210	0.7	40	207	0.7	39

15 to 20 K/min. Frequency factor is also found to increase with increasing heating rates. The values of $\ln Z$ obtained by both the techniques were seen to lie in the same range. This may be explained in terms of transformation from diffusion controlled kinetics to decomposition governed kinetics.²⁷ Diffusion of degraded product takes place at lower heating rate and consequently, lower kinetic parameters are observed. On the other hand, degradation of polymer is faster at higher heating rate resulting in higher kinetic parameters.¹⁰ Both Friedman and Chang techniques showed consistent results of PHDDA degradation kinetics.

Kinetic study of PHDDA by Kissinger and Ozawa techniques using multiple heating rates

In nonisothermal decomposition techniques, the Kissinger and Ozawa methods are used to determine the kinetic parameters which require multiple heating rates. The Kissinger method is capable of evaluating all average kinetic parameters like activation energy; frequency factor, and order taking different heating rate into account, whereas Ozawa technique provides information regarding the activation energy of the system as a function of conversion.

The Kissinger plot of PHDDA system is shown in Figure 6(a). The estimated activation energy from this method is 170 kJ/mol. The order of the decomposition and collision factor has been determined as 1.0 and 28.6 min^{-1} , respectively.

The Ozawa plots obtained for different conversions of PHDDA are shown in Figure 6(b). The slope of $\ln q$ vs. $1/T$ gives the apparent activation energy. The regression of the linear fit lies in the range of 0.982–0.998, which is well within the acceptable range. The activation energies calculated for different conversions are listed in Table II. It is found that in low conversion around 6–10%, the activation energies increases slowly from 149 to 163 (kJ/mol) and as the conversion progresses further from 14 to 80%, the activation energy varies from 169 to 225 kJ/mol. Tables I and III indicate that this method is quite consistent with Friedman and Chang techniques after 10% conversion. This trend in change of activation energy with conversion also suggests that there are two mechanisms governing the degradation process of PHDDA. At lower conversion, PHDDA degrades in bulk with random chain scission and at higher conversion chain end scission

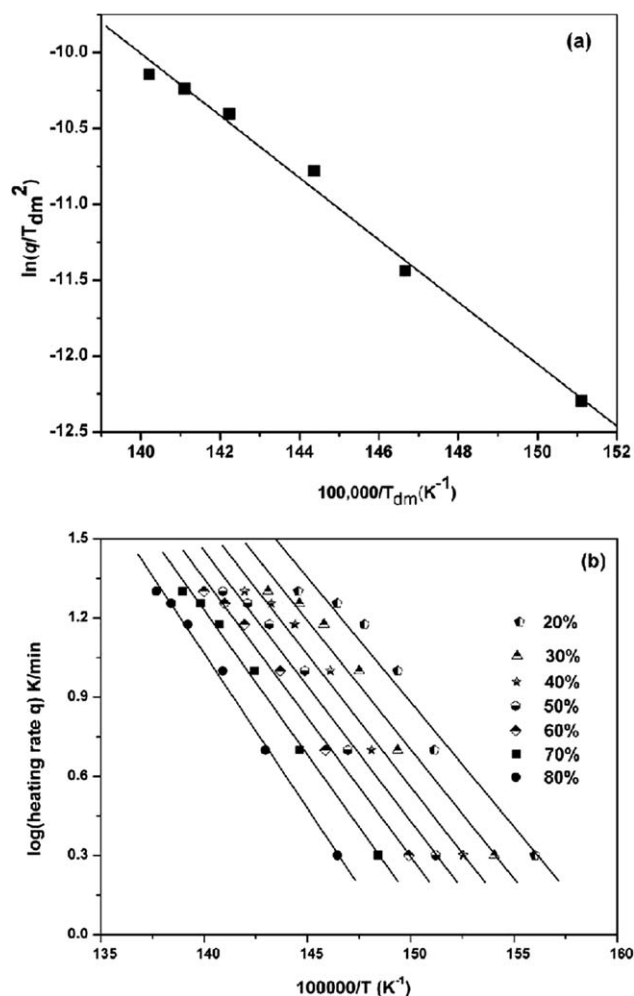


Figure 6 (a) First Kissinger Plot (b) Ozawa plot for thermal degradation of PHDDA.

dominates the process which is similar to the thermal degradation of polycaprolactone.²⁸ Using the above techniques, it is evident that Kissinger technique is used by averaging all the heating rates where conversions are not involved. Friedman and Chang methods are based on conversion at single heating rate. On the other hand, Ozawa technique takes into account both conversion and multiple heating rates together, which indicates reliability of this method. Our study shows that the result from Friedman and Chang methods are acceptable at 10 K/min heating rate with Ozawa technique after 20% conversion. This indicates that the Friedman and Chang methods which avoid multiple heating rates experiments can be used to evaluate kinetic parameters for poly(HDDA-co-MMA).

TABLE II
Kinetic Parameters of Thermal Decomposition of PHDDA for Different Conversion Evaluated by Ozawa Technique

Conversion (%)	6	8	10	12	14	20	30	40	50	60	70	80
E_a (kJ/mol)	149	155	163	167	169	172	178	183	187	192	200	215

TABLE III
Kinetic Parameters of Various Composition of Poly(HDDA-co-MMA) at Single Heating Rate Using Friedman and Chang Technique

Sample code	Friedman			Chang		
	E_a (kJ/mol)	n	$\ln Z$ (min^{-1})	E_a (kJ/mol)	n	$\ln Z$ (min^{-1})
PHDDA	176	0.9	34	180	1.0	34
Phpm7525	147	0.6	31	156	0.6	31
Phpm5050	101	0.4	23	111	0.4	23
Phpm2575	100	0.4	21	107	0.4	23
PMMA	124	0.8	25	133	1.0	28

Kinetic study of poly(HDDA-co-MMA) by single heating rate

The kinetic parameters of poly(HDDA-co-MMA) of various compositions have also been determined by Friedman and Chang techniques using single heating rate. The Friedman and Chang plots of the blends of different composition at 10 K/min heating rate are shown in Figure 3(a,b), respectively. It is seen from Table III that there is drop in the values of kinetic parameters (i.e., activation energy, order, and frequency factor) of the blend with increasing PMMA content in the system. PMMA shows higher activation energy and order than the blend of Phpm5050 and Phpm2575 compositions, but the thermal stability of PMMA is found to be lesser than all poly(HDDA-co-MMA) blends, as is evident from the T_{25} , T_{50} , T_{75} compositions from Figure 3(a,c). This is because the order of the reaction also changes in PMMA and the copolymer of poly(HDDA-co-MMA). The order of stability is in the following sequence PMMA < Phpm2575 < Phpm5050 < Phpm7525 < PHDDA, which indicates that PMMA is least stable, whereas PHDDA is the most stable and other copolymer have intermediate stability.

Debinding studies

The above kinetic studies revealed that at lower heating rate, the reactions are diffusion controlled. Because the debinding kinetics is diffusion governed process,⁹ lower heating rate has to be adopted during binder removal. To examine the rate of binder removal through isothermal degradation, at isothermal TGA of PHDDA has been performed at six different temperatures from 350 to 400°C at a step of 10°C. The TG curves obtained at different temperatures are shown in Figure 7(a). The plot shows that PHDDA exhibits moderate and steady decomposition at 350°C and 360°C and loses 40% and 38% of its initial weight at 150 min. The decomposition rates are significantly enhanced above 380°C temperature. Applying the Flynn technique eq. (11), a set of five straight lines were obtained from the plot between $\ln(t)$ vs. $1/T$ for corresponding fractional weight loss ranging from 10 to 45 wt %. The isothermal curves

between $\ln(t)$ vs. $1/T$ are shown in Figure 7(b). The regression of all the lines are ~ 0.99 . The apparent activation energy and $\ln Z$ are evaluated for respective conversions from the slope and intercept of the straight lines and are listed in Table IV. It has been observed that E_a and $\ln Z$ remains almost constant around (146 ± 3 kJ/mol) and (26 ± 1) min^{-1} , respectively. Lower activation energy evaluated from Flynn technique shows that this process also progresses through diffusion of degraded product. The objective of the work is to deduce the activation

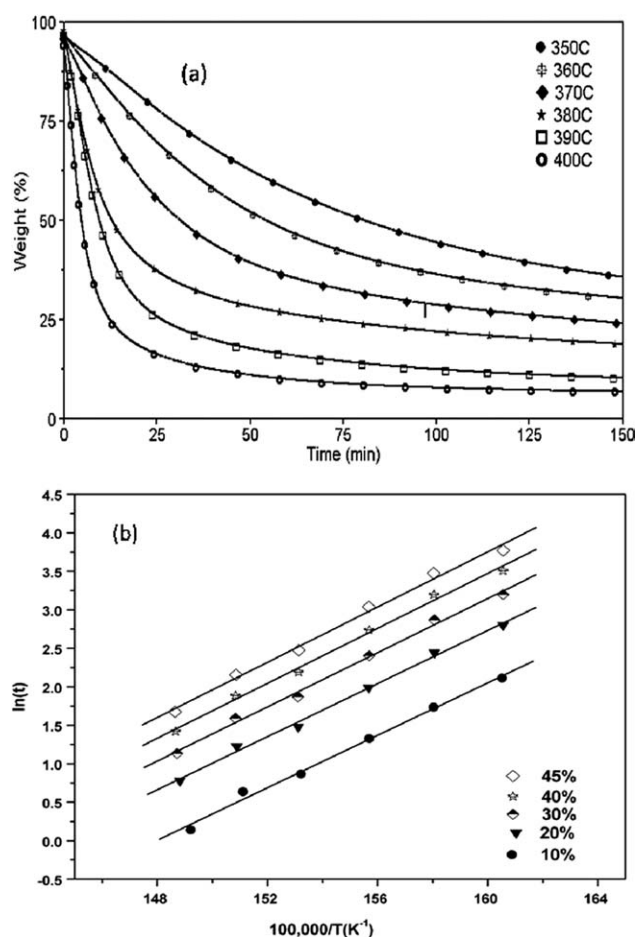


Figure 7 (a) Isothermal decomposition of PHDDA at different temperature, (b) corresponding Flynn plot at different conversion.

TABLE IV
Kinetic Parameters of Isothermal Decomposition of PHDDA at Various Isothermal Temperatures Using Flynn Technique

Weight loss (wt %)	10	20	30	40	45
E_a (kJ/mol)	142	143	146	148	149
$\ln Z$ (min^{-1})	28	26	26	26	25

energy so as to maintain it as diffusion controlled process. On the other hand, it is seen that with increasing content of MMA in poly(HDDA-co-MMA), the kinetic parameters reduced indicating the process approaches the diffusion governed kinetics. The thermal stability in all the compositions is equally important so as to provide the green strength to the ceramic body. TGA curve shown in Figure 3(a) indicates that Phpm5050 has an optimum thermal stability and degrade through diffusion controlled process at 10 K/min heating rate. Therefore, it can be suggested that debinding operation can be done by three ways. PHDDA homo polymer can be removed by either heating at low rate or at normal heating rate (10 K/min) up to 10% removal followed by isothermal degradation or by choosing a composition, e.g., Phpm 5050 that can be degraded through diffusion controlled reaction using normal heating rate.

We also investigate whether the degradation should be carried out in air or nitrogen. The DTA curve shown in Figure 8 indicates that degradation of PHDDA in air has multiple exothermic peaks in the range from 360 to 450°C temperature which may result in localized heating in ceramic body like hot spot, delamination or anisotropic shrinkage.⁹ However, the presence of two weak endothermic peaks in presence of nitrogen atmosphere for both PHDDA and its blend with PMMA indicates that N₂ atmosphere is a better option during debinding operation.

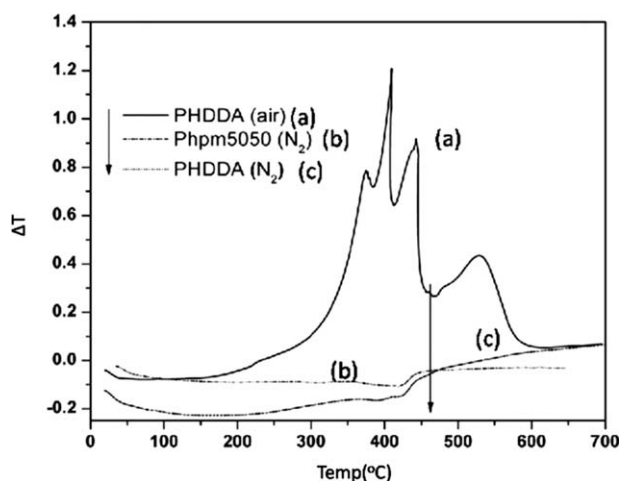


Figure 8 DTA plot of Poly (HDDA-co-MMA) blend at 10 K/min heating rate in N₂ and air atmosphere.

CONCLUSIONS

Thermal degradation of PHDDA and its blend with PMMA have been studied by following different models of thermal analysis to determine its debinding kinetics. All the compositions studied through DSC suggested the formation of copolymer. The kinetic parameters evaluated from nonisothermal single heating rate by Friedman and Chang techniques for PHDDA system are in acceptable range. Kissinger method showed an average kinetic value which is in agreement with Friedman and Chang technique in low heating rate, whereas the kinetic values obtained by Ozawa method is found to match with both of these methods with respect to conversion and heating rate. Therefore, Friedman and Chang techniques are useful to evaluate kinetic parameters thereby avoiding the need of multiple heating rate experiments. Flynn technique, which has been used for the isothermal heat treatment of PHDDA, indicates that kinetic parameters are almost in constant regime with increasing weight-loss fraction indicating the degradation is through diffusion process. In case of poly(HDDA-co-MMA) compositions, Friedman and Chang methods have been adopted to determine the kinetics, which is found to decrease with the increasing MMA content in the copolymer. The developed Phpm5050 copolymer composition has been shown to have an effective debinding ability without sacrificing the green strength of ceramic material during binder burn-out.

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