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Heat Resistance of Polymers

Oxidative decomposition and Thermal decomposition

1. Introduction

Thermogravimetry (TG) can be used to evaluate the decomposition temperature and the quantification of components, since the decomposition of a material caused by heat is accompanied by a mass change. Especially for polymeric materials, TG measurement is widely used to evaluate the heat resistance and thermal stability of various polymeric materials and it is adopted in various testing standards such as ISO, ASTM, JIS, and IPC.

The decomposition of polymers can be broadly classified into oxidative decomposition and thermal decomposition. Oxidative decomposition is a decomposition in which molecular chains are cleaved by oxidation reactions in an atmosphere containing oxygen such as air, and finally gasification occurs. Thermal decomposition is a decomposition in which the molecular structure is broken by thermal energy in an inert atmosphere. Since the mechanism of decomposition differs greatly between oxidative decomposition and thermal decomposition, it is necessary to select an appropriate atmosphere according to the purpose when measuring the decomposition of polymer materials by TG.

In this report, we introduce examples of TG measurements of oxidative and thermal decomposition of polyamide 6 (N6), polyimide (PI), low-density polyethylene (LDPE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polycarbonate (PC), polystyrene (PS), polytetrafluoroethylene (PTFE), polypropylene (PP), and polymethyl methacrylate (PMMA).

2. Measurements

The polymer samples used for the measurement were all commercially available materials.

TG measurements were performed using the NEXTA STA200 Thermogravimetry Differential Thermal Analyzer, with oxidative decomposition measurements performed under an air and thermal decomposition measurements performed under a nitrogen atmosphere. Table 1 shows the measurement conditions, which were made referring to ISO[1)], ASTM[2)], JIS[3)], and IPC[4,5)].

Table 1 Measurement Conditions

	Oxidative decomposition	Thermal decomposition
Atmosphere	Air	N_2
Flow rate	200 mℓ/min	
Sample mass	10 mg	
Sample pan	Pt open pan	
Temperature range	Ambient to 800 °C*	
Heating rate	10 °C/min	

* Measured up to 900 °C for polyimide.

3. Measurement Results

3-1 Oxidative decomposition measurement

Since most of the polymer used as industrial materials are used under an air environment, oxidative decomposition measurements in an air atmosphere are generally used to evaluate the heat resistance and thermal stability of materials. Figure 1 shows the TG measurement results of each polymer in an air atmosphere. It can be seen that the initiation temperature of mass loss due to decomposition and the behavior of the decomposition process differ depending on the type of polymer.

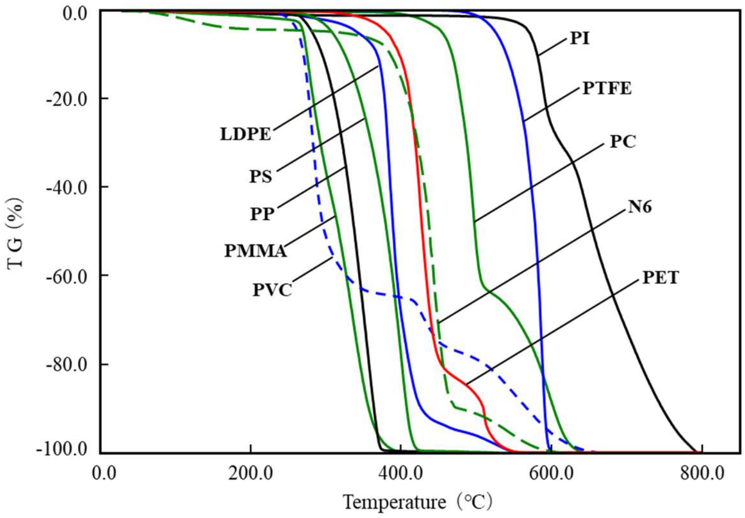

Figure 1 TG curves for each polymers in Air

3-2 Thermal decomposition measurement

In order to understand the basic thermal properties of each material itself, thermal decomposition measurements under an inert atmosphere using TG were performed. Figure 2 shows the TG measurement results of each polymer under N_2 atmosphere. As in Figure 1, the initiation temperature of mass loss due to decomposition and the behavior of the decomposition process differ depending on the polymer.

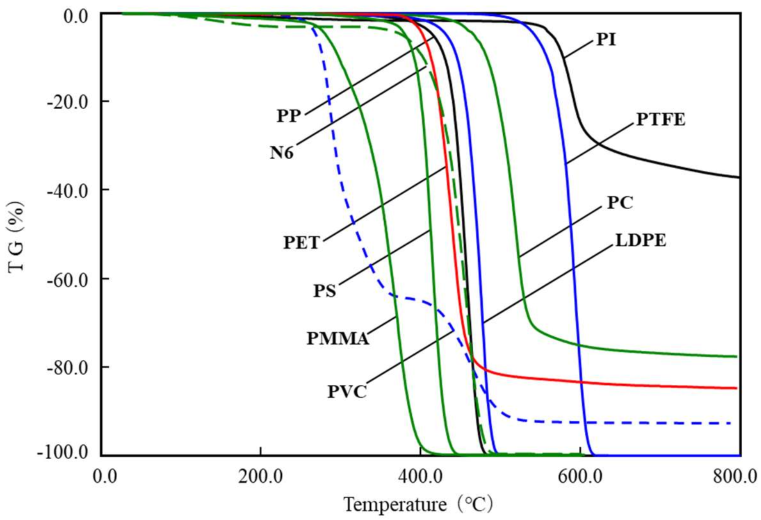

Figure 2 TG curves for each polymers in N_2

3-3 Decomposition mechanism of Polymers

In the measurement results of oxidative decomposition in an Air (Figure 1), all polymers fully decompose during heating up to 800 ºC. On the other hand, in the measurement results of thermal decomposition under N_2 (Figure 2), some polymers did not. While oxidative decomposition measurement observes decomposition caused by oxidative reaction with oxygen in the Air, thermal decomposition is a very complicated mechanism in which multiple reactions progress simultaneously. And polymers that remain carbon in the decomposition process will not decompose by 100 %.

Figure 3 shows an example of classification of thermal decomposition patterns[6)]. Thermal decomposition can be broadly classified into gas-forming and carbon residue types. The gas-forming type is a decomposition in which the main chain is cleaved by thermal energy, resulting in a decrease in molecular weight and ultimately a gas-forming. The carbon residue type is a decomposition in which the main chain is broken by thermal energy, but some or many parts are carbonized, and residual carbon is produced. The measurement results in Figure 2 show that PVC, PET, PC and PI do not 100 % decomposed, indicating that carbon residue type decomposition is occurring.

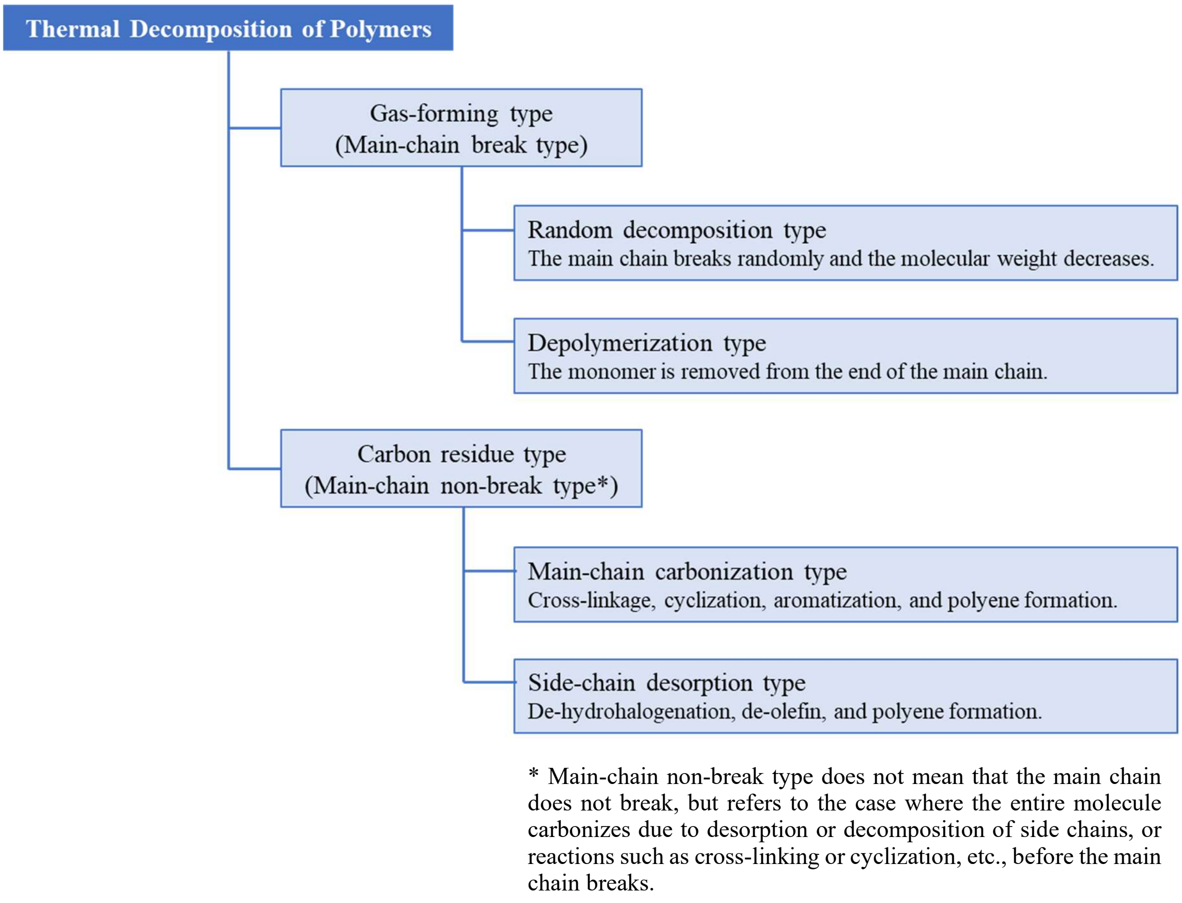

Figure 3 Classification of thermal decomposition patterns[6)]

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On the other hand, the decomposition rate of PMMA, PS, N6, PP, LDPE, and PTFE in Figure 2 was 100 %. It indicates that gaseous product type decomposition occurred. These are cases in which the main chain is broken and decomposes, main chain cleavage type, and it is thought that this decomposition occurs because the bonds in the main chain are forcibly broken by thermal energy. Therefore, the higher the bond-breaking energy, the bond dissociation energy, of a polymer, the less likely it is to undergo thermal decomposition, and the bond dissociation energy of a polymer can be used as a guide to predict the ease or difficulty of thermal decomposition[7]. As an example, Figure 4 shows the results of plotting the relationship between the mass loss initiation temperature T_i and the bond dissociation energy D_0 of PMMA, PS, PP, PE, and PTFE in Figure 2, which were read by the method of ISO standard[1]. The higher the bond dissociation energy of the main chain shows, the higher the mass loss initiation temperature becomes. In other words, it has high heat resistance to thermal decomposition.

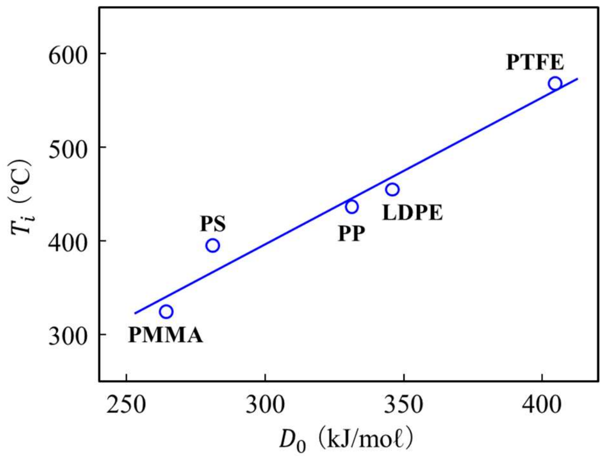

Figure 4 Relationship between T_i and D_0 for PMMA, PS, PP, LDPE and PTFE

Reference

1) ISO 11358-1 Plastics -- Thermogravimetry (TG) of polymers - Part 1: General principles, International Organization for Standardization (2014)
2) ASTM E2550 - 17 Standard Test Method for Thermal Stability by Thermogravimetry, American Society for Testing and Materials (2017)
3) JIS K 7120 Testing Methods of Plastics by Thermogravimetry, Japanese Industrial Standards Committee (2020)
4) IPC-TM-650 2.3.40 Thermal Stability, Association Connecting Electronics Industries (1995)
5) IPC-TM-650 2.4.24.6 Decomposition Temperature (Td) of Laminate Material Using TGA, Association Connecting Electronics Industries (2006)
6) J. Mukai, N. Kinjo, Practical Polymers, Kodansha (1981)
7) H. H. G. Jellinek (ed.), Aspects of Degradation and Stabilization of Polymers, Elsevier (1978)