A detailed bond stretch model of thermal decomposition

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Abstract: Thermal decomposition is caused by the breaking of the bonds of polymer chains after they are stretched to a length threshold. Any factors that affect the bond stretch can affect the thermal decomposition process. The physical processes like glass-transition changes and the physical configuration of the polymer chains affect the stretch mechanism apparently. Thus, glass-transition and molecular weight may be reflected in the thermal decomposition process characterized by the thermogravimetric (TG) or differential thermogravimetric (DTG) curves. This idea was confirmed by the thermal decomposition of solid poly-α-methyl styrene (PαMS).

The experiment results showed that the DTG curves change suddenly near the glass-transition temperature, and the activation energy goes up with an increase of molecular weight, which indicates that the physical process is vital in the thermal decomposition process.

1. Introduction

In the thermal decomposition process, solid polymer may go through complex physical and chemical processes. Usually, only the chemical processes like bonding and breaking are considered and studied by traditional chemical dynamic method used for homogeneous system [1-3]. However, physical processes tend to be crucial [4] in the solid polymer decomposition processes.

One of the important physical processes that polymer goes through is glass-transition, which causes remarkable chain configuration changes in a short time. Some polymer materials have a relatively high glass-transition temperature under which the thermal decomposition is already underway. The glass-transition temperature of Poly-α-methyl styrene (PαMS) is up to 192°C [5] and an observable weight loss during thermogravimetric analysis starts around 170°C according to Ye [6]. This makes the PαMS a possible material for the investigation of the impact of glass-transition and hence the chain configuration of polymer thermal decomposition. Such effect is seldom studied. On the other hand, the thermal decomposition is widely studied by thermogravimetric (TG) or differential thermogravimetric (DTG) method. If the impacts of glass-transition on thermal decomposition are evident, there may be some sudden change in TG or DTG curve around glass-transition temperature, which makes TG or DTG method a potential useful experimental way to locate the glass-transition temperature.

Another important factor that affects the physical configuration of the polymer chains is molecular weight, which on the one hand affects the glass-transition temperature and on the other causes more complex entanglement between chains. In the thermal decomposition study of PαMS [7], the activation energy goes up with an increase in molecular weight from 188 to 272 kJ/mol. The influence is evident.
In section 2, we propose two physical models to describe the different bond breaking mechanisms for glass and high elastic phase polymers. In section 3, this work is summarized.

2. Theory and application

For an amorphous polymer, as the temperature goes up, the polymer leaves the glassy phase and turns into high elastic phase suddenly. In glassy phase, the movement (like rotation) of polymer chain segments is forbidden, while in high elastic state some chain segments that get enough energy are moveable. This change causes a large expansion of the phase space of the polymer chain and happens in a tiny temperature range. Therefore, a small temperature change during glass-transition can cause apparent change of polymer physical performance (specific volume, refractive index, diffusion coefficient, etc.) [8]. On the other hand, the influence of molecular weight is evident in thermal decomposition process [7]. Thus, it is worth discussing whether and how the thermal decomposition performance is affected by the physical processes and finally establishing a model to describe them uniformly.

2.1. The thermal decomposition model for glassy phase polymer

In glassy phase, the movement of chain segments is forbidden; all atoms are vibrating near equilibrium position. The polymer material is like a three-dimensional wire entanglement. The structure configuration of every polymer chain is fixed. For a specified main chain with n units, the energy corresponding to a particular structure can be simplified as a function of bond length \( r \) and bond orientation (in three-dimensional) \( \theta \) noted as \( U(r_1, r_{n-1}, \theta_1, \ldots, \theta_{n-1}) \). A small structure change compared to equilibrium position will create an energy change of

\[
\Delta U = \sum_{i=1}^{n-1} \frac{\partial U}{\partial r_i} \Delta r_i + \sum_{i=1}^{n-1} \frac{\partial U}{\partial \theta_i} \Delta \theta_i + \ldots, \tag{1}
\]

which means the energy change is strongly affected by the original structure. It is worth noting that the structure change \( (\Delta r_1, \ldots, \Delta r_{n-1}, \Delta \theta_1, \ldots, \Delta \theta_{n-1}) \) caused by thermal excitation is not independent. The bond and orientation coordinates are not canonical coordinates so the particular form of \( U \) with initial condition is needed to determine the correlation of \( (\Delta r_1, \ldots, \Delta r_{n-1}, \Delta \theta_1, \ldots, \Delta \theta_{n-1}) \). However, one can infer that the changes of various bond lengths will differ from one another when stretching the bonds of the main polymer chain by thermal excitation. Each change meets a certain distribution according to the equilibrium structure configuration.

2.2. The thermal decomposition model for high elastic phase polymer

In high elastic state, some chain segments that get enough energy are moveable. The movement makes some chain segments softer and reduces the differences among bonds. An energy change caused by thermal excitation can spread over the bonds of the segment more easily and therefore more equally, which differs notably from the case of glassy phase. On the other hand, the segment movements (like torsion and slippage) are correlated with the chains around it; when the temperature goes up the interactions between surroundings and chains are weakened. The movements like torsion and slippage become easier. Thus, even in the high elastic phase, the physical configuration is still in evolution.

It is worth noting that the movements of chain segments (torsion, slippage, stretching, etc.) are correlated. The existence of torsion and slippage may affect the stretching apparently. An explicit proof of the correlation of slippage and stretching is found in the fracture process and the mechanics of polymer bearing a macroscopic applied force. The fracture can be caused by two reasons, one is the bond breaking of main chain, and the other is slippage [9]. The former happens in the low temperature range while the latter happens in the high temperature range. The same applied force applied on
different slippages may cause different stretching results (with or without bond breaking). In the thermal decomposition process, the thermal excitation can be treated as random applied forces on the polymer chain, thus the bond breaking mechanism in the macroscopic situation is a very good reference for its thermal decomposition counterpart. In the glass-transition process, the free volume effects and hence the torsions could have something to do with the slippage and stretching correlation.

2.3. The thermal decomposition during glass-transition

During glass-transition, the number of moveable chain segments increases suddenly. Thus, the thermal decomposition behaviour changes suddenly according to the mechanism change as described above. This sudden change is observed in the DTG experiment as shown in the Fig. 2 of [6]. One can figure out that there is an inflection at around 185 OC, which is very near the glass-transition temperature of PtMS (180OC or 192 OC). Another observation comes from the DTG study of polyvinyl chloride (PVC) as illustrated in the Fig. 8 of [2]. There is a bump in the DTG curve at around 90°C, which is near the glass-transition temperature of 85°C [10] of polyvinyl chloride. It is noteworthy that the bumps we found in the DTG curves may due to some other processes, including thermal decomposition process. For example, the free volume effects due to glass-transition may open many new escape channels for the impurity molecules and cause a fluctuation in the TGA study. A lot of works have to be done to confirm which reason is predominant. However, the situations in poly-α-methyl styrene and polyvinyl chloride show that the glass-transition does affect the DTG curve and the influence is observable. The DTG method could be used to detect the polymer glass-transition temperature and the mechanisms are definitely worth exploring. The bond stretch model is an interesting possibility.

2.4. The molecular weight dependence in thermal decomposition

The fact that activation energy goes up with molecular weight [7] indicates that the thermal decomposition process is highly affected by the conformation of chain structure (physical process), since the bond strength difference may not be apparent in polymers with different molecular weights. This can be explained by our bond stretch model since any factors that affect the bond stretch can affect the thermal decomposition process. The interchain interactions affect the segment motions like torsion, slippage and stretching, and are more complicated as the molecular weight goes up. The correlation of these motions may finally affect the bond breaking (caused by random stretching) of thermal decomposition process.

3. Conclusion

The bond stretch model gives a clear picture and hence qualitative analysis of the physical processes involved in thermal decomposition process. Any factors that can affect the bond stretch (like glass-transition, molecular weight) can affect the thermal decomposition process. Base on this model, this paper explains the DTG observation that the structure and movement of chain segments can affect the bond stretch and hence the decomposition process, and suggests that the DTG method could be used to detect the polymer glass-transition temperature when polymer’s decomposition and glass-transition process coexist in a certain temperature range.

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