Thermal properties, degradation and stability of poly(vinyl chloride) predegraded thermooxidatively in the presence of dioctyl phthalate plasticizer

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Abstract

Thermooxidative degradation of poly(vinyl chloride) (PVC) is inevitable during processing of PVC. Recycling of this polymer requires reprocessing in most of the cases, and due to the low thermal stability of PVC, it is of paramount importance to reveal the effect of thermooxidation on the thermal stability of this commercially important polymer. However, detailed systematic investigations are lacking on this crucial problem. In this study, the thermal behavior of PVCs thermooxidized in dilute dioctyl phthalate (DOP) (di(2-ethylhexyl) phthalate, DEHP) plasticizer was investigated by DSC, thermal gravimetry and isothermal degradation under inert atmosphere. It was found that thermooxidation leads to PVCs with certain extent of internal plasticization by DOP chemically bound to the PVC chains and by the oxidized chain segments as well. Thermogravimetry and isothermal dehydrochlorination under inert atmosphere revealed that even low extent of thermooxidation of PVC (0.4 mol% of HCl loss in 30 minutes at 200 °C) leads to dramatically decreased thermal stability of this polymer with 50-60 $^{\circ}$C lower onset decomposition temperature than that of the virgin resin. This unexpected finding means that at least part of the oxidized moieties formed during oxidation of the PVC chains acts as initiators for thermal dehydrochlorination at relatively low temperatures, resulting in significant decrease of the thermal stability of the polymer. These striking results also indicate that the decreased thermal stability caused by thermooxidation in the course of the primary processing of this polymer should be taken into account in order to efficiently stabilize PVC products for reprocessing and recycling.

1. Introduction

Poly(vinyl chloride) (PVC) is one of the most widely used commercial polymers. It is produced in the third largest amount among polymers in quantities over 35 million tons per year worldwide. Its increasing production and use is mainly due to the availability of cheap starting materials, economic production and board application possibilities from soft rubbery to hard materials, and in part to its safe storing capacity of chlorine, harmful to the environment and health, which is produced simultaneously with NaOH by salt electrolysis in very large quantities (1,2). However, the increasing demand for PVC has led to the problem of handling more and more PVC waste. Disposing used PVC products to the landfill increases the amount of permanent waste because it does not break down in the environment. Incineration and pyrolysis of this polymer requires significant circumspection due to the elimination of corrosive HCl by heat from the PVC chain and to the potential formation of toxic substances. Therefore, recycling of PVC wastes has become a central problem of polymer science and technology in recent years (see e.g. Refs 3-9 and references therein). However, reprocessing of already processed and used PVC arises several fundamental problems, especially the effect of structural changes that occur in the polymer chain during the primary processing and the subsequent use of the polymer products on its thermal stability and degradation behavior.

It is well-known that in addition to the advantageous properties and versatility of PVC, it has poor thermal stability and severe degradation may occur even at processing temperatures and during applications (see e.g. Refs. 1,10-26 and references therein). It is noteworthy that although the thermal degradation of PVC and its composites in inert

atmosphere has been widely studied since the second half of the last century, the mechanistic details of this process has not been revealed fully yet. It is well established that the primary process of PVC degradation is the zip-elimination of HCl and simultaneous formation of conjugated double bond containing sequences (polyenes) in the polymer backbone (10-17). It is also known that in addition to initiation of this degradation process by slow elimination of HCl from regular vinyl chloride monomer units in the chain (10-12), allylic and tertiary chlorine containing defects, as proved by degradation of PVCs with deliberately introduced amounts of such irregularities (10,11,18,19,38-42), have significant contribution to the thermal instability of this polymer. However, conclusive evidence is still lacking whether the thermal zip-elimination of HCl in inert atmosphere takes place by molecular, ionic or radical mechanisms. The termination mechanism of this chain reaction is also unclear. Above the processing temperature, the thermal decomposition (pyrolysis) of PVC occurs in two major steps. First, HCl eliminates from the polymer in conjunction with the simultaneous formation of polyenes in the chain accompanied with the evolution of low amounts of volatile organic compounds up to about 330 $^{\circ}$C (20-29). In the second step above this temperature, the breakdown of the remaining material leading to various compounds takes place (27-30). Investigating this process by thermal gravimetry has been widely used for determining the thermal stability of a large variety of PVC mixtures, composites and products (see e.g. Refs. 20-29 and references therein). However, while intensive research has been carried out on thermogravimetry with primary PVC products and corresponding experimental samples, only few studies have dealt with the thermal analysis of recycled PVCs (21-23). The results of the existing investigations clearly indicate the complexity of the degradation process of such PVCs, because of the

different kinds of additives and processing conditions commonly used for PVC production have significant influence on the degradation reactions, thus on the stability of PVCs considered for reuse and reprocessing during recycling.

Surprisingly, there is an important aspect which is usually not considered in the thermal analyses of PVC products at all. This is the effect of oxygen on the structural changes of PVC occurring during processing or in the course of sample preparation in air, such as roll milling, ball milling, calendering, extrusion, blowing, injection molding, curing, pressing etc. Taking into account such effects might be cumbersome not only in data evaluation but in processing and especially recycling of PVC wastes as well. In the latter case, the thermal stability of the recycled PVCs is of paramount importance for the reprocessing and application possibilities of such materials. These changes occur in the case of every PVC products processed in air, so it is very surprising that according to the best of our knowledge systematic investigations on the thermal behavior and stability of PVCs which underwent thermooxidation has not been reported yet at all. The reasons may be connected to the difficulties of data evaluation arising from solid sample preparation which results in ill-defined effects of different parameters, such as the effect of the pretreatment, mechanical degradation, preoxidation, inhomogenities, the presence and the effect of additives etc. Then, the inseparable superposition of the different effects of the prehistory of the sample determines the thermal behavior of the PVC samples. Therefore, our approach tries to avoid these sample preparation problems, and PVC samples pretreated in dilute solution were investigated, and thus such studies can be considered as model experiments that may open the road to investigations of more complex systems, such as PVCs manufactured according to industrial recipes. Exploring the degradation and stabilization of PVC in dilute solutions

has already been applied by us, and such studies have provided several fundamental results on the initiation of degradation of PVC (10-12) and led also to the formulation of the reversible blocking mechamism of PVC stabilization (13,14).

In a previous study (31), we have shown that thermooxidative degradation of PVC in dilute dioctyl phthalate (DOP) (di(2-ethylhexyl) phthalate, DEHP), the most widely used plasticizer for PVC, leads to severe chain scission (even to oily products) and partially oxidized PVCs under mild conditions in oxygen atmosphere at 200 $^{\circ}$C as analyses of the thermooxidized polymer by gel permeation chromatography, FTIR and NMR spectroscopies indicated. Since the large majority of PVC production takes place in air at around this temperature, the resulting PVCs obtained in this process might be considered as model polymeric materials to gain substantial information on the effect of thermooxidative treatment, such as processing in the industrial practice, on the thermal stability of such PVCs. Herein, we report on our unprecedented findings on the effect of thermooxidation of PVC in a plasticizer on its thermal behavior.

2. Experimental

2.1. Materials

A suspension PVC (S5070) (Borsodchem Ltd., Hungary) and dioctyl phthalate (DOP) (Aldrich, 99 %) were used in our experiments. DOP was purified by passing through a chromatography column of neutral alumina. Tetrahydrofuran (puriss.) and hexane (96 %) (Molar Chemicals Ltd., Hungary) were used as received.

2.2. Sample preparation

The PVC samples were treated in dilute (1% w/v) dioctyl phthalate (DOP) solutions in oxygen with a flow rate of 5 dm^3/h at 200 °C for different times as described

previously (31). After this thermooxidative degradation process, the samples were precipitated first from DOP then from THF into n-hexane to remove the residual phthalate. Finally, the precipitated samples were dried to constant weight under vacuo at room temperature.

2.3. Analysis methods

The evolution of free HCl was monitored on-line with a Metrohm PVC Thermomat 763 instrument. The degradation temperature was 200 °C under both nitrogen and oxygen with a flow rate of 5 dm^3/h.

Molecular weight distributions (MWD) and average molecular weights were determined by gelpermeation chromatography (GPC). The GPC was equipped with a Waters 515 HPLC pump, PLgel 5 mm Mixed-C column set (Varian) and a dual RI and viscosimetry detector (Viscotek). THF was used as eluent with 1 mL/min flow rate. Calibration based on polystyrene standards was used to calculate the MWD of polymers.

A Varian Scimitar 2000 Fourier transform infrared spectrometer equipped with an MCT (Mercury-Cadmium-Telluride) detector and a single reflection 'Golden Gate' ATR accessory (with diamond ATR element) was used to perform IR measurements.

The DSC measurements were carried out by a Mettler DSC 30 instrument from -120 °C to +120 °C with 10 °C/min heating rate. The second heating scan was evaluated.

Thermal analysis measurements (TGA) were performed on a Mettler Toledo TG50 Tc 15 under nitrogen flow from 35 °C to 750 °C at 10 °C/min heating rate. The evaluating software was Star^e SW 9.30.

3. Results and Discussion

Processing at elevated temperatures and use of PVC take place in air, that is in the presence of oxygen. Therefore, the influence of these effects, especially thermooxidation, on the thermal stability of PVC for a variety of applications and especially for reprocessing in the course of recycling should be taken into account. However, surprisingly systematic studies on this phenomenon cannot be found in the literature. Due to the importance of such fundamental knowledge, especially in respect of the increasing demand for recycling of PVC, we aimed at investigating the consequence of thermooxidation of this polymer on its thermal behavior. In order to avoid the inescapable difficulties arising from preparation of solid samples, such as inhomogeneities, mixing, curing, mechanical effects etc., predegraded PVC samples were obtained by thermooxidative degradation in dilute solution of dioctyl phthalate (DOP), the most widely used industrial plasticizer. DOP is used in huge amounts in polymer industry, thus large quantities of PVC waste with dioctyl phthalate content should be handled not only nowadays but in the future as well. Therefore, investigating the effect of thermooxidation of PVC in the plasticizer on its thermal properties is expected to result in fundamental information which can be utilized in the course of processing, applications and recycling of such materials. As recently reported by us (31), this process yields elimination of HCl with the formation of chromophoric structures in the chain, partial oxidation of the polymer, chemical coupling of low amounts of DOP to the chain, and last but not least remarkable chain scission of PVC. The evolution of free HCl as a function of time in this thermooxidative process is shown in Figure 1. Samples with degradation times of 0.5, 1, 1.5, 2 and 3 hours were prepared. The molecular weight data and polydispersities of the resulting degraded polymers are

shown in Table 1. As these data indicate, thermooxidative degradation of PVC under the applied mild conditions results in relatively rapid chain scission in the absence of detectable cross-linking as previously reported by us (31). The partial oxidation of PVC is proved by the difference between the FTIR spectra of the starting and degraded PVCs as displayed in Figure 2. The increase of the carbonyl and hydroxyl bands with maxima of 1728 cm^{-1} and 3460 cm^{-1}, respectively, clearly shows the formation of such structural units in the chain during thermooxidation (32). As detailed NMR analyses of PVCs thermooxidatively degraded in DOP indicated, low amounts of DOP chemically bounds to the PVC chain during this process (31).

First, differential scanning calorimetry (DSC) experiments were carried out with a series of oxidatively predegraded PVC samples (the samples are denoted with the degradation times). The DSC curves of the starting PVC and the thermooxidatively treated PVCs are shown in Figure 3. It is evident from this Figure that oxidation of PVC and/or coupling of the DOP plasticizer to the polymer chains result in the decrease of the glass transition temperature (T_g), that is thermooxidation of PVC in DOP yields internal plasticization of the polymer. Similar results were reported by Reinecke et al. (33) on chemically phthalated PVC, but in this case phthalate-based thiol additives had to be prepared first by a multistep reaction route. Our degradative modification is a one-pot, simple process under mild conditions. As shown in Table 1 and Figure 4, the T_g of the PVC decreases by ~14 $^{\circ}$C even after 30 minutes thermooxidative treatment. Increased reaction times up to about 1.5 hours does not result in further decrease of T_g. Longer degradation times yield PVCs with further decrease of T_g, by ~22 $^{\circ}$C for the sample oxidized in DOP for 3 hours. This decrease of the glass transition temperature upon thermooxidation in DOP can be attributed to both the DOP coupled to the polymer

chains and to the effect of partially oxidized polymer segments as internal plasticizers. These findings indicate that PVC degraded during processing in air might have significantly lower T_gs than that of the starting materials. This effect might be useful for reprocessing purposes.

Undoubtedly, one of the major properties of PVC is its thermal stability which is a determining factor not only for the primary processing but also for reprocessing during recycling. Therefore, comparative thermogravimetry (TG) was carried out under nitrogen with the untreated starting PVC and with the samples obtained by thermooxidation in DOP at 200 °C for different times. As the thermogravimetric curves of the investigated samples show in Figure 5, the partially oxidized PVC samples start to decompose at remarkably lower temperatures than that of the starting PVC. The onset temperatures (T_{onset}) of decomposition in Table 2 reveal that there is about 50-60 °C decrease in the start of the degradation process as a result of thermooxidative predegradation. As shown in this Table, a short reaction time (30 mins), i.e. low extent of thermooxidation corresponding only to 0.4 mol% HCl evolution as shown in Figure 1, leads already to dramatic decrease of the T_{onset} value by 50 °C. On the basis of these striking results, it can be concluded that even low level of oxidation during processing and use may lead to significant decrease of the thermal stability of PVC. Taking into account the existing results on the thermooxidative degradation process of PVC (11-14,31,32,34-37), it can be considered that decomposition of peroxides formed by oxidation of polyenes and the main chain might be predominantly responsible for the lower decomposition temperatures of the thermooxidized polymers. As reported earlier (11,14,34-37), initiation of zip-elimination of HCl by radicals formed by oxidation of polyenes is the

major factor which results in higher rates of PVC degradation under thermooxidative conditions than that of under inert atmosphere.

In Figure 5, it can also be seen that the decomposition of all the PVC samples occur in two distinct stages in accordance with literature data (see e.g. Refs. 11,20-28). In the first step, mainly HCl eliminates form the chain and simultaneously some other, lower amounts of volatile compounds are also formed (11). This is well indicated by the fact that the weight loss in this first stage is larger that that expected by exclusive quantitative HCl loss during this phase (the weight loss corresponding to quantitative HCl loss from the starting PVC is indicated by the dashed line in Figure 5). In the second stage, the increase of the temperature leads to the breakdown of the material remaining after the first phase of decomposition.

In order to have a better insight into the degradation behavior of thermooxidized PVCs, the thermogravimetric (TG) and differential thermogravimetric (DTG) curves are plotted in Figure 6 separately for each sample. Comparing these curves and the data in Table 2 for the temperature values of the first minima (T_{m1}), indicating the maximum decomposition rates, it can be seen that there is a significant shift to lower temperature values upon thermooxidation by about 20-40 ^{o}C, and T_{m1} decreases with increasing oxidation time. Thus, the T_{m1} values also confirm the remarkable decrease of the thermal stability of PVCs with thermooxidation prehistory. The DTG curves also indicate that a rapid decomposition is followed by a slower degradation process with lower amplitude. This latter corresponds mainly to the formation of volatile compounds by secondary processes of the polymer in the chain (11). As Figure 6 and the temperature (T_{f}) of the minimal decomposition rate between the two main degradation steps indicate, the second stage of decomposition starts at 371 ^{o}C for all the samples with the exception of

the 3h sample with a somewhat lower value of 365 ^{o}C. This result indicates that independent of the thermooxidative pretreatment, the thermal degradation in the first stage yields very similar structures in all cases. This is also corroborated by the temperature values of the highest decomposition rate in the range of 450-460 ^{o}C for all the samples. The effect of the oxidative predegradation, i.e. the HCl loss during this process, is also reflected by the differences between the extents of weight loss ($\triangle m_1$) in the first stage of degradation. The differences between the $\triangle m_1$ values of the preoxidized and untreated PVCs increase with the reaction time of the thermooxidative pretreatement. This is in line with the fact that the higher the reaction time of thermooxidation, the higher the extent of HCl loss in this process as shown in Figure 1.

Isothermal dehydochlorination experiment was also carried out with the untreated polymer and a thermooxidized PVC (2h) in nitrogen atmosphere at 200 ^{o}C. The extent of HCl elimination as a function of time is shown in Figure 7. The rate of HCl loss of the thermooxidized PVC is significantly higher than that of the starting, untreated polymer. This is an additional proof for the decrease of thermal stability of PVC upon thermooxidation.

Conclusions

In industrial practice, processing of PVC takes place in the presence of air at elevated temperatures leading to inevitable thermooxidation of the polymer to certain extents. In order to study the effect of this process on the thermal stability of PVC, which is of paramount importance in relation to effective stabilization for processing and especially reprocessing during recycling, the thermal degradation of PVCs treated thermooxidatively in dilute DOP solutions was investigated by thermogravimetry and

isothermal degradation. These experiments resulted in the striking observation that even low level of thermooxidation (0.4 mol% HCl evolution in 30 minutes at 200 $^{\circ}$C) leads to the dramatic decrease of thermal stability of PVC. These findings indicate that thermooxidation results in new, thermally labile structural sites which initiate thermal dehydrochlorination of PVC with higher rates at significantly lower temperatures than that of present in the untreated polymer. It has to be emphasized that our unprecedented results on the significant decrease of thermal stability of thermooxidized PVCs also indicate that special care should be exercised in relation to the stabilization for PVC processing, and especially in the case of recycled PVCs for reprocessing purposes.

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Table 1. The number and weight average molecular weights and the polydispersity (M_w/M_n) of the starting polymer and PVCs thermooxidized to different times.

Thermooxidation time (hour)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
0 (PVC)	81600	171700	2.10
0.5	32700	49400	1.51
1	20700	28900	1.40
1.5	14600	21500	1.47
2	11200	15800	1.41
3	6600	10700	1.62

Table 2. The glass transition temperature (T_g), the onset temperature (T_{onset}), the temperature of the maximum rate of decomposition in the first degradation stage (T_{m1}), the temperature of the minimum rate of degradation between the two stages (T_f), and the weight loss in the first (Δm_1) and second (Δm_2) degradation steps.

Sample	T_g/ °C	T_{onset} / °C	T_{m1} / °C	T_f / °C	Δm_1 (%)	Δm_2 (%)
PVC	86.6	221	293	371	64.4	26.6
0.5 h	72.2	171	270	371	62.7	25.7
1 h	72.7	164	257	371	62.0	27.6
1.5 h	73.6	164	257	371	61.6	27.8
2 h	68.6	171	250	371	60.0	26.2
3 h	63.9	178	250	365	60.7	25.9

FIGURE CAPTIONS

Figure 1. Extent of free HCl evolution (X_{HCl}) as a function of time in thermooxidatiive degradtion of PVC solution in dioctyl phthalate(1% w/w PVC in DOP, oxygen, 200 °C).

Figure 2. Fourier transform infrared spectra of the starting PVC and PVC thermooxidized for 2 hours.

Figure 3. The differential scanning calorimetry curves of the starting PVC and the PVC samples treated under thermooxidative conditions for different times.

Figure 4. The glass transition temperatures (T_g) of the starting PVC and the thermooxidize PVCs as a function of reaction time.

Figure 5. The thermogravimetric curves of the starting PVC and the PVC samples treated under thermooxidative conditions for different times (N_2 and 10 °C/min heating rate; the weight loss corresponding to quantitative HCl loss from the starting PVC is indicated by the dashed line).

Figure 6. The thermogravimetric and difefrentila themogratvimetric curves of the starting PVC and the PVC samples treated under thermooxidative conditions for different times (N_2 and 10 °C/min heating rate).

Figure 7. The extent of HCl evolution (X_{HCl}) as a function of time in thermal degradtion of the starting PVC and the PVC sample thermooxidized for 2 hours (solid PVC samples, nitrogen atmosphere, 200 °C).
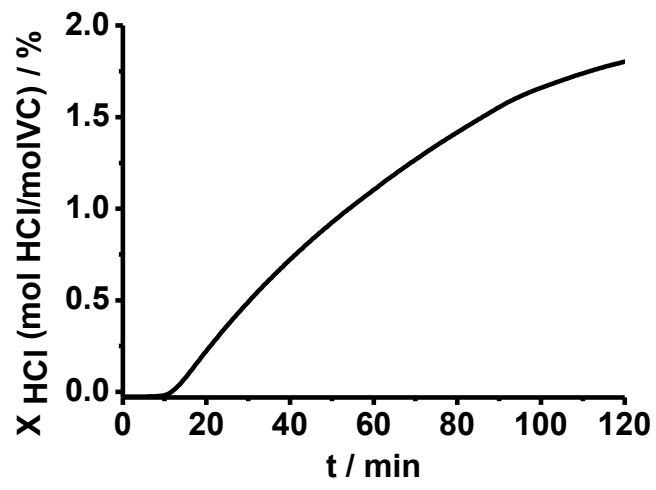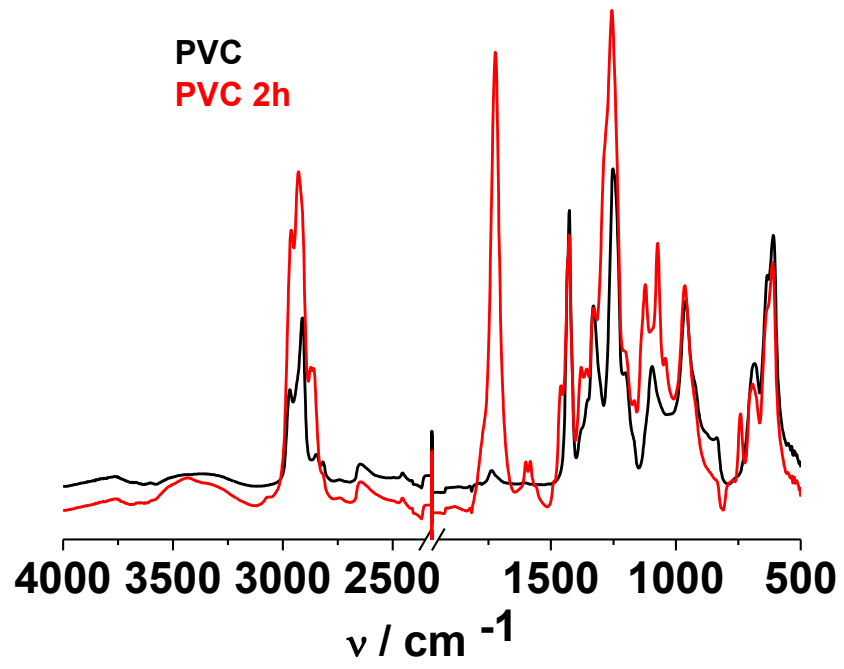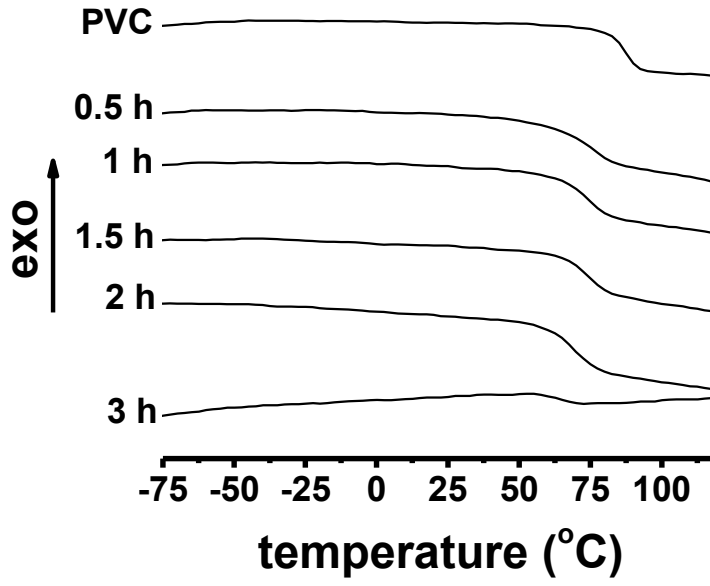
Figure 1

Figure 2

Figure 3

Figure 4
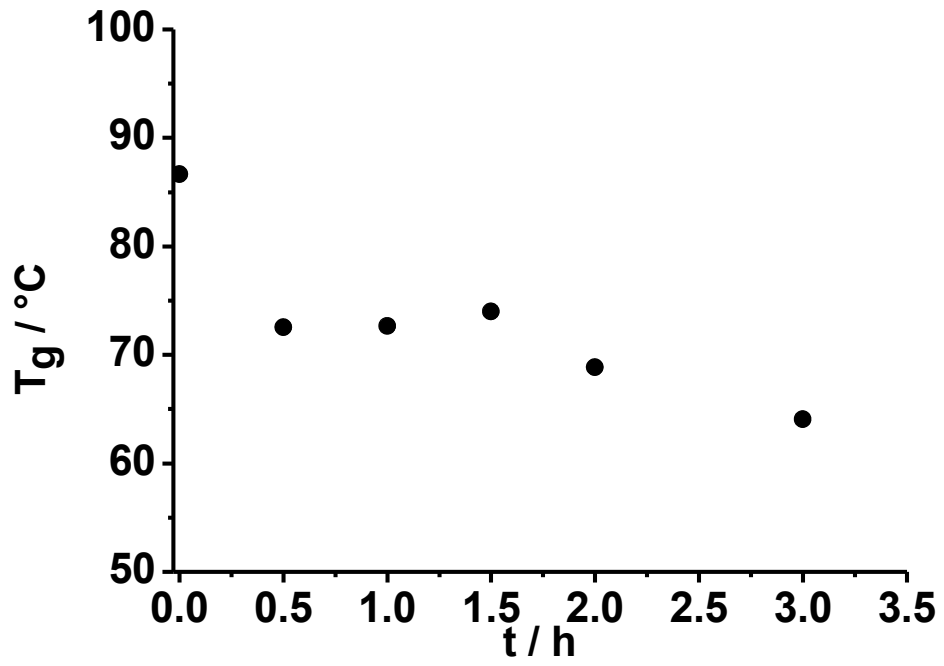
Figure 5

Figure 6

Figure 7