

Decomposition of Poly(ethylene glycol) in Nanocomposites

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ABSTRACT: Poly(ethylene glycol) (PEG) has been widely used in studies of polymer–clay nanocomposites because it readily intercalates in smectite clays. Nanocomposites were formed from PEG with molecular weights (M_w) ranging from 300 to 20,000, as evidenced by expansion of the basal planar spacing of the clay (d_{001}) in X-ray diffraction. However PEG with high molecular weight ($\geq 10,000$) readily underwent degradation during preparation of composites when heated at low temperature (60°C) due to oxidative attack. Molecular weight distribution determined by gel permeation chromatography showed that this degradation always happened with or without the presence of clay and it

became more serious when the molecular weight was higher. The reduction in pH of aqueous PEG solutions after degradation increased with molecular weight. Since d_{001} was independent of molecular weight over a wide range, such degradation cannot be detected by this method. Precautions against oxidative attack are therefore recommended to avoid decomposition when preparing PEG–clay nanocomposites. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 548–552, 2004

Key words: poly(ethylene glycol); degradation; nanocomposites; molecular weight distribution; clay

INTRODUCTION

Poly(ethylene glycol) (PEG) is a nonionic, polar, water-soluble polymer. It has been widely used in many fields such as lubricants, pharmaceuticals, cosmetics, surfactants,^{1–3} and as a biodegradable reagent in metal extraction.⁴ In polymer–clay nanocomposites, there is also active research interest in such polymers [designated PEG or poly(ethylene oxide) (PEO)]⁵ for the development of rechargeable batteries.^{6–13} The problem of degradation in this context has not been reported, although ample evidence^{1–3,14–21} shows that PEG undergoes decomposition under some circumstances at very low temperatures. This study draws attention to the fact that the decomposition problem can also persist in PEG–clay nanocomposites.

There are three major methods for making polymer–clay nanocomposites: the common solution method, melt-processing methods, and *in situ* polymerization. The first involves mixing polymer with clay suspension in a solvent for the polymer and heating at an appropriate temperature for intercalation. In the second, the polymer melt is directly intercalated in the clay galleries. The third involves inserting monomer (and initiator if necessary) into clay galleries by mixing and then heating the mixture to cause polymerization. This work used the solution method.

Montmorillonite is a type of smectite clay that is frequently used in polymer–clay nanocomposites. Its crystal structure is made up of units composed of two silica tetrahedral sheets fused in an alumina octahedral sheet. When a polymer molecule is polar, such as PEG, it can penetrate (intercalate) into the untreated clay galleries, causing the lattice to expand in the *c* direction,²² increasing the basal planar spacing, d_{001} , and forming an “intercalated” polymer–clay nanocomposite. In this case, clay not only adsorbs polymer on its external surface but also absorbs it in internal galleries. Such clays are sometimes designated “swelling clays.” Other types of clay can only adsorb polymers, even polar polymers, on the external particle surfaces, of which kaolinite is a typical example. Processing this clay with most polymers leads to a “conventional composite” rather than “nanocomposite.” This work studied the decomposition characteristics of PEGs under those processing conditions that are often used in solution methods^{23–25} for preparing polymer–clay nanocomposites.

EXPERIMENTAL

Reagent grade PEGs with nominal average molecular weights (M_w) of 8,000 and 12,000 (denoted PEG8000 and PEG12000) from Alfa Aresa (Germany); a similar grade denoted PEG35000 with 2-*tert*-butyl-4-methoxyphenol as stabilizer from Merck Eurolab (Germany); and PEGs with MWt of 300, 600, 1,500, 4,000, 6,000, and 10,000 from BDH Laboratory Supplies (Poole, UK) were used. The sodium montmorillonite (type: BH

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natural) was generously supplied by Black Hills Bentonite LLC (Wyoming, USA) having a density of 2,600 kg/m³ and the kaolinite was kindly donated by Charles B. Crystal Co., Inc. (New York, USA) with a density of 2,580 kg/m³.

PEG–clay nanocomposites were prepared using the solution method: 5 g montmorillonite was added to 100 mL distilled water and agitated for 5 h on a roller table to prepare clay suspension. PEG with a range of M_w was individually added to clay suspension (PEG : clay = 0.7 by mass) and mixed for a further 5 h. The mixture was heated in an oven at 60°C for 24 h. The resultant products were ground into fine powder for X-ray diffraction (XRD) to check intercalation. XRD was carried out on a Siemens D5000 diffractometer (40 kV, 40 mA) with CuK α radiation ($\lambda = 0.154$ nm). The slits were set as 0.1°, with steps of 0.02° and a scan time of 2.5 s per step.

To assess the decomposition in the absence of clay under similar conditions to those experiments when such polymers are converted into polymer–clay nanocomposites, PEGs with different M_w were dissolved in distilled water (3 g PEG in 100 mL) and dried in an air-circulating oven at 60°C for 24 h. The M_w distribution difference of PEG before and after dissolution and drying was studied using gel permeation chromatography (GPC) employing tetrahydrofuran with antioxidant as the solvent and columns of Polymer Laboratories PLgel 2 x mixed bed-D (30 cm, 5 μ m). The nominal flow-rate was 1.0 mL/min. The system was calibrated with narrow molecular weight distribution PEG calibrants and the data were collected and analyzed using Viscotek Trisec 2000 and Trisec 3.0 software by Rapra Technology Limited (Shrewsbury, UK).

The pH values of aqueous solutions of the PEGs before and after dissolution and drying were compared using a JENWAY 3051 pH meter (BDH Gelplas, Dorset, UK) and pH papers (BDH Ltd, Dorset) as a confirmation of the pH range. The pH meter was calibrated using buffer solutions of pH 4 and 7. The concentration of the PEG solution was 1M for the repeat unit, i.e., 4.4 g/100 mL. These measurements were carried out at a temperature of 18°C.

To assess the decomposition of PEG in the presence of clay, the nonswelling kaolinite was used instead of montmorillonite to avoid the complexity of preferential intercalation.²⁶ 1.5 g of PEG4000 and 1.5 g PEG35000 were added together to 100 mL kaolinite aqueous suspension (0.05 g/mL), which was mixed for a further 5 h. Samples were centrifuged (Centaur 2, DJB Labcare, Bucks, UK) at 4,200 rpm for 44 h. Sediment and supernatant were dried separately in an air-circulating oven at 60°C for 24 h. The amount of free polymer in the supernatant was found gravimetrically. Molecular weight distribution of PEGs was determined using GPC with the same setting and procedure as described above.

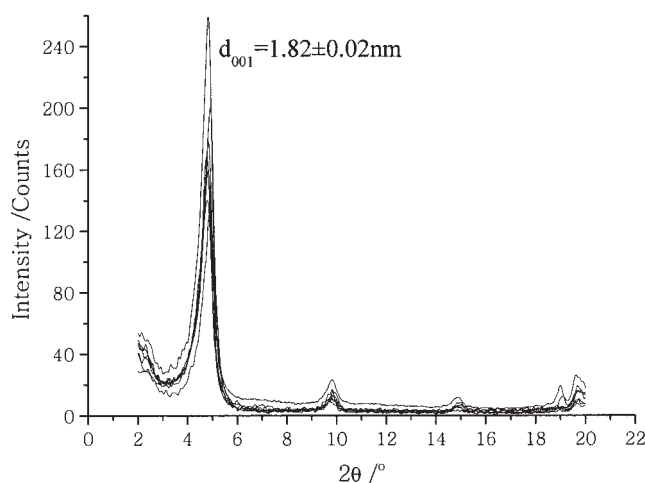


Figure 1 XRD patterns for PEG–clay nanocomposites (PEGs with M_w of 300, 600, 1,500, 4,000, 6,000, 10,000, and 20,000).

RESULTS AND DISCUSSION

The PEGs used in the preparation of PEG–clay nanocomposites spanned a large range of molecular weight, from 300 to 20,000 and, in each case, XRD, which indicates intercalation by increase of d_{001} , showed that a nanocomposite had formed. The results are shown in Figure 1. The d_{001} of the montmorillonite was increased from 1.23 to 1.82 ± 0.02 nm in each case, irrespective of polymer molecular weight.

Figure 2 shows the molecular weight distributions of PEGs as received and those after dissolving in distilled water and drying at 60°C for 24 h. It indicates that only PEG4000 and PEG8000 were stable after this mild treatment. The number of chain scissions per molecule B is given by:^{27–29}

$$B = \frac{\bar{M}_n(0)}{\bar{M}_n(t)} - 1$$

The values of B were 0.34, 0.80, and 1.21 for PEG10000, PEG12000, and PEG20000, respectively, which is in agreement with the literature^{3,30} which shows that the degradation of PEG increases with molecular weight and the scissions are not totally random as determined from GPC molecular weight distribution. It is worth noting that different polymerization routes are available for these polymers. For PEG or PEO with a M_w up to about 10,000, EO is generally polymerized by an anionic polymerization method in the presence of an initiator (typically sodium hydroxide) or starter such as alcohol, ethylene glycol or its oligomer, or water.³⁰ For high M_w PEO, heterogenous initiator systems (mainly alkaline earth compounds or organometallic compounds) are used for the polymerization.^{30,31} This polymerization is generally thought to occur through

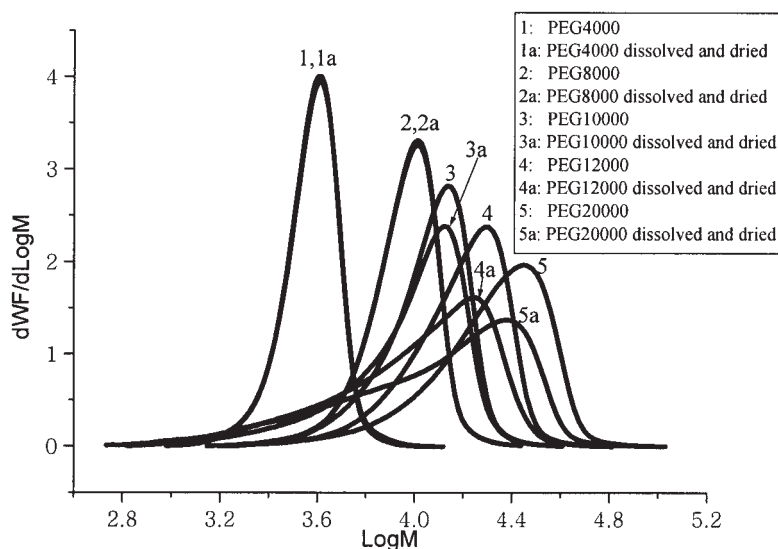


Figure 2 Molecular weight distribution for PEGs before and after dissolution and drying.

a coordinated anionic mechanism, in which EO is coordinated to the initiator through an unshared electron pair on the oxirane oxygen atom.³¹ The polymerization method or residues therefore may affect the degradation. Indeed, high M_w PEO calibrants in GPC are rather unstable despite refrigerated storage.

In addition to PEG with M_w greater than 10,000, those with lower M_w have also been found to undergo degradation under certain conditions,^{3,14,15} such as higher temperatures, higher oxygen partial pressures, or longer times, beyond those used in preparing nanocomposites.

The decrements of pH value for $M_w = 10,000$, 12,000, and 20,000 were 0.14, 0.25, and 0.38, respectively, indicating that acids are products of the degradation reactions. It was found that PEG underwent oxidation to form mainly oligomers and short-chain acids under wet conditions and to form esters instead of acids under dry conditions.^{3,14} One of the proposed mechanisms¹⁴ is as shown in Scheme 1.

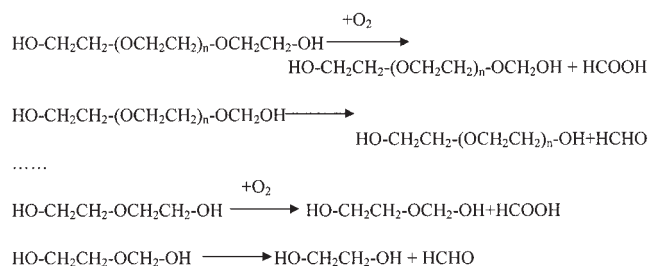
Under dry conditions, short-chain acids, e.g., formic acid, are trapped by the remaining PEGs to give esters. However, under the wet condition, the acid derivatives cannot be found because of the constant presence

of water and the acidic environment formed in the reaction solution, so only successively smaller PEGs and free short-chain acids are formed. In addition to mono(short-chain) acid derivatives, di(short-chain) acid derivatives also appear as the dry reactions proceed.

There is another interpretation for the formation of short-chain esters under dry conditions.³ This mechanism suggests that PEG reacts with oxygen to form α -hydroperoxide, which then decomposes according to a radical mechanism. These two hypothesized mechanisms for the dry reaction are relevant when melt-processing PEG-clay nanocomposites, which is also a common method of preparation.³²

With water as solvent, the degradation of PEG produces acids that decrease pH value. The more extensive the degradation, the more the pH value decreases, supporting the proposed mechanism of PEG degradation under wet conditions. The decrease noted here is comparatively lower than the reported values³ of around 4, because of the lower heating temperature and lower oxygen pressure imposed on the PEG.

To study the decomposition of nondegradable ($M_w < 10,000$) and degradable PEGs ($M_w \geq 10,000$) in the presence of clay simultaneously, a mixture of PEG4000 and PEG35000 was used. Figure 3 shows the M_w distributions of PEG4000, PEG35000 and their mixtures after dissolution and drying with and without the presence of kaolinite. The peak for PEG4000 remained almost the same after dissolution in water and drying while PEG35000 underwent slight degradation like other PEGs with a $M_w \geq 10,000$. The curves *b* and *c* overlapped and their M_w data are shown in Table I. Within measurement error, the M_w of the PEG mixture remained the same with and without the presence of kaolinite.



Scheme 1

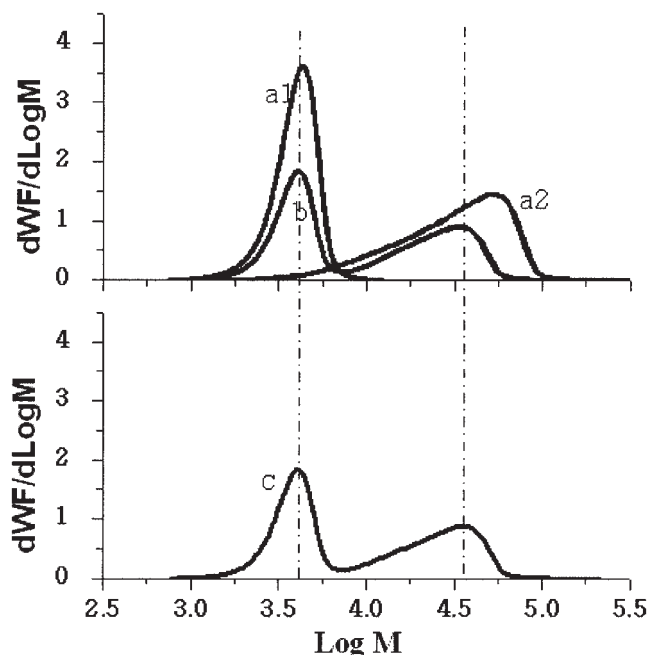


Figure 3 Molecular weight distribution for (a1) PEG4000; (a2) PEG35000; (b) a mixture of PEG4000 and PEG35000 (1 : 1) after dissolution and drying; and (c) the dried supernatant of PEG4000/35000 after sedimentation of kaolinite.

Most literature ascribes the degradation of PEG to an oxidation mechanism but some conclude that this degradation is due to a thermal mechanism²⁰ or even to high-speed stirring,¹⁶ although PEG was exposed to air in that work. In the field of polymer-clay nanocomposites, it may be important to consider oxidation of PEG.^{13,33,34} In preparation, such nanocomposites can be heated at 80°C in air, which could cause the degradation of PEG as discussed above. The ionic conductivity may thus be affected by degradation.

Most PEG-clay nanocomposites are prepared either via solution methods^{6-9,23,35} or using melt-processing methods.^{9-13,35-37} The former ideally requires a vacuum oven to dry the aqueous suspension of PEG and clay to avoid the possibility of degradation. There are two approaches to melt-processing of nanocomposites: pressing the polymer-clay mixture at room temperature, followed by annealing in a vacuum oven or an oven filled with inert gas at a temperature higher than the glass transition point (T_g) or the melting point (T_m) of the polymer^{9,10,37} or heating the mixture in the melt to allow the polymer to migrate into clay galleries.^{11,33} The latter route often uses a device that exposes the mixture to air, e.g., a twin-roll mill. According to the literature,¹⁹ serious oxidation of PEG takes place at temperatures higher than T_m compared to slight degradation when the temperature is lower than T_m . Studies¹⁸ show that T_g of PEG undergoes little change with oxidation even after 3 days, due to the

recombination of free radicals formed during the reaction, so that T_g measurement is also a poor guide to degradation. Dynamic mechanical testing however shows that the area under the loss factor curve increases arising from the increased amorphous content of the polymer with progressive oxidation. Therefore, with degradable PEG, melt-processing in air is not recommended.

CONCLUSION

PEG-montmorillonite nanocomposites can be prepared with a wide range of M_w spanning from 300 to 20,000, in which d_{001} was increased to the same value (~ 1.82 nm) irrespective of molecular weight. A nonswelling clay, kaolinite, was selected to avoid the confounding factor of differential molecular weight segregation into the galleries. Decomposition occurred to the same extent in the presence or absence of clay. The degradation rate increased with M_w , probably due to the different polymerization method, and caused more acidity in the PEG solution with greater M_w .

The experiments presented here highlight the difficulties in research on PEG-based nanocomposites because of the decomposition problem, which could lead to ambiguous assessments of composite properties but would not affect d_{001} , the usual indicator of composite formation. Experiments should be carefully designed to prevent polymer degradation even at low temperatures ($< 100^\circ\text{C}$).

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TABLE I
GPC Molecular Weight Data for PEGs

Sample ^a (Designation as in Figures 2-3)	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
PEG4000	3,740	3,660	1.02
PEG4000 ^a	3,770	3,680	1.03
PEG8000	9,130	8,610	1.06
PEG8000 ^a	9,100	8,510	1.07
PEG10000	11,600	10,300	1.1
PEG10000 ^a	10,300	7,660	1.4
PEG12000	16,000	13,400	1.2
PEG12000 ^a	12,100	7,440	1.6
PEG20000	22,400	17,000	1.3
PEG20000 ^a	15,400	7,690	2
PEG35000	36,800	26,800	1.4
PEG4000/35000 ^a	15,400	6,080	2.5
PEG4000/35000 ^b	15,700	6,050	2.6

^a PEG after dissolution and drying.

^b The dried supernatant of PEG4000/35000 after sedimentation of kaolinite.

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