SYNTHESIS AND MECHANICAL PROPERTIES OF POLYURETHANE/MONTMORILLONITE NANOCOMPOSITES

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Keywords: polyurethane, PTMG, PC, MMT, mixed polyol, prepolymer, undersea-cable protector

1 Introduction
Polymer/clay nanocomposites where nanoscale silicate layers are molecularly dispersed within the polymeric matrix exhibit dramatic concurrent enhancements of mechanical, thermal stability, flame retardancy, and barrier properties even when employing small loading levels of clay(<10 wt%) when compared to pure polymer[1]. Therefore, since such nanocomposites were reported by the Toyota group, more research has been done in this field[2]

To make polymer/clay nanocomposite, reform MMT by alkyl-ammonium ions react with Na+MMT. Already research is reported that alkyl chain length is increase in alkylammonium, modified MMT widen the space between the layers.[3,4]

Manufacture nanoparticle composite exist three type of synthesis method. First is Polymerization method that insert monomer in the modified MMT. Second is Melting insert method that the polymer in melt condition insert in the modified MMT. Third is compounding method that a very Small amount of melting condition polymer insert to modified MMT and then mechanical mixed with large amount polymer.[4,5,6] The manufactured nanoparticle composite like this method, classified exfoliated nanoparticle and intercalated nanoparticle. Exfoliated nanoparticle is that silicate layers are completely desquamation from polymer matrix and dispersed by way of single layer. Intercalated nanoparticle is that polymer insert to between the silicate layers because of silicate layer distance increase, but dispersed in polymer matrix by way of few multiply silicate layer.

In particular, polymer and organic modifier in silicate nanocomposites in exfoliated nano-composites mechanical properties such as tensile strength and modulus improved and heat distortion temperature is increasing, as well as gas barrier, flame retardancy excellent. Therefore, for the preparation of exfoliated nanocomposites has been a lot of research.

2 Experimental
2.1 Materials and sample preparation

Na+-MMT Kunimi Co.(Japan) Kunipia F was purified using. PTMG(Poly(tetramethylene glycol)) and PC(Polycarbonate diol) ARDRICH Company’s products were purchased(MW=2000) 1,4 BD(1,4-butandiol) ARDRICH Company’s products also are used to.

2.2 Sample preparation and characterization

Octadecyl trimethyl ammonium bromide and the reaction of Na+-MMT, ODTMA-MMT has been synthesized and cleaning(ethanol:water=1:2) and centrifugation. To be purified by vacuum drying at room temperature for 24 hours ODTMA-MMT, get the hydrophobic MMT, and used next reaction. ODTMA-MMT prepared in the amine group of the silicate layers, ODTMA-MMT dispersed in toluene 6hr, APS for silane coupling reagent clay/APS=:13 ratio is added and reacted in a nitrogen atmosphere 48hr(APS-MMT). 40g of toluene heated to 110°C and PU-graft-maleicanhydride 10g dissolved, APS-MMT 2g dispersed in 20g toluene by mixing the solution reacted 48hr(PU-MMT). Polyurethane synthesis was divided into two step. First step, packed into the reactor under a nitrogen atmosphere and then mixed polyol & same moles MDI agitated 80°C,100rpm,6hr. next step, NCO-prepolymer reach a certain level of viscosity in excess of the MDI, PDMS, 1,4-BD and the
addition of modified MMT 4hr after the stirring in the same environment. The excess MDI is used chemical crosslink[7]

Using X-ray diffraction, Na⁺-MMT, APS-MMT, ODTMA- MMT, PU-MMT, and X-ray diffraction patterns of the nanocomposites were obtained. Sample for TEM, PU and embedding regant capsule placed with in next 24hr and then polymerized at 60°C, using a diamond cutter attached microtoner cut thickness into about 70–90nm were obtained. Using the tensile tester with varying strain rate was increased by the 50 mm/min, each measure 10 sample were obtained from the average.

3 Result and discussion

Typically, organic chain length increase of alkyl groups of inserted into MMT interlayer, MMT interlayer distance increase. In this study, the organic alkylammonium ions such as octadecyl trimethyl ammonium ions using a modified internal of Na-MMT, MMT in the interlayer of the pu-graft-maleicanhydride PU derivatives through the reaction was performed to insert. Fig.1 MMT of the modified in order to determine the interlayer distance was observed by XRD. Na-MMT, the interlayer distance of silicate know that there are 13.3 Å, ODTMA-MMT silicate interlayer distance of 22.3 Å Na- MMT by 9.1 Å than the interlayer distance is increased up to find. The silicate interlayer distance increase because of ODTMA insert to Na-MMT interlayer. And APS-MMT interlayer distance of the ODTMA-MMT and can see almost the likeness, which APS & ODTMA molecular occupied similari size by the MMT interlayer.

Na-MMT, ODTMA-MMT and APS-MMT IR spectrum was schematically in Fig.2. C₁₈H₃₇N(CH₃)₃⁺ ions into a Na-MMT could not see the other bands were observed in ODTMA-MMT. And with respect to the layered silicates found in 1040cm⁻¹ near the band are not significantly different before and after the reaction could be obtained, which is layered silicates have been the reaction showed that the maintainence. Another of the layered silicate information can be obtained through solid-state ²⁹Si MAS NMR, Fig.3 it was on the schematic. Q⁵(Si(OSi)₃(O,H)) and Q⁴(Si(OSi)₄) of MMT caused by the signal -93.5 ppm appear in the vicinity, it does not change after the reaction was found. But that is generated by reaction with APS the MMT T(₂H₂NPr-Si(OSi)₁(Ο,ΟH), T(₂H₂NPr-Si(OSi)₂(Ο,ΟH)), meaning the signal was in the vicinity of -66.2 ppm. This it means substituted trimethyl ammonium group Si, and through which APS,MMT by the reaction of amine that is known to be grafting. To make exfoliated nanocomposite, PU-MM & PU mechanical mixing and observing by XRD, the results shown in Fig.4 In the case of PU-MMT, MMT interlayer distance is 20.5 Å, APS-MMT interlayer distance the front and you can see the likeness. Fig.4(b) is PU-MMT&PU nanocomposite material by mechanical mixing, you can see not have characteristic peak. This mean that sample become exfoliated nanocomposite.

Next, the mechanical properties of nanocomposites prepared PU, respectively, PU in nanocomposites than pure elongation has shown that approximately 32% reduction, the tensile strength of about 20%, and 2.4 times increased up young’s modulus can be seen. PU in nanocomposites tensile strength and elongation were decreased compared to the pure PU. This is ,MMT dispersed in PU polymer influence , considered.

4 Conclusions

Na-MMT is modified by octadecylammonium ion, that case MMT interlayer distance increased, for amine insert, APS insert to modified MMT and observed by solid-state NMR, MMT interlayer distance has no effect was negligible. In addition, APS-MMT react with PU-graft-maleicanhydride , PU derivatives was inserted in MMT’s interlayer and confirmed by FT-IR. This mechanical mixture with PU, XRD observed in characteristic peak of MMT had gone to see, that distributed in single layer on PU matrix, that confirmed.

In other words, MMT layers is distributed as a single layer in PU matrix, exfoliated nanocomposite could be prepared.
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Figure 1. XRD pattern of (a) Na-MMT, (b) ODTMA-MMT, and (c) APS-MMT

Figure 2. FT-IR spectrum of (a) Na-MMT, (b) ODTMA-MMT, and (c) APS-MMT

Figure 3. Solid-state $^{29}$Si-NMR spectra of (a) APS-MMT, (b) ODTMA-MMT, and (c) Na-

Figure 4. XRD patterns of (a) PU-MMT and (b) PU nanocomposite.
References