

MODIFICATION OF NYLON-6 WITH POLYORGANOSILOXANE

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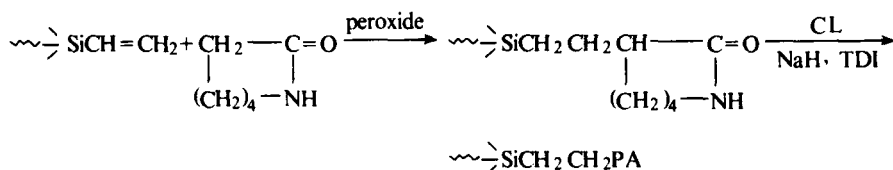
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ABSTRACT

Nylon-6 has been modified by polyorganosiloxane. It was realized by radical addition of caprolactam to the vinyl group of silicone and anionic polymerization of the monomer in the presence of the silicone macromer. The mechanical properties of the modified plastics are not far from that of the unmodified one whereas its frictional properties are significantly improved.

Polyamide plastics is one of the engineering materials with high strength, high stiffness and many other good properties widely used as automobile parts, electrical components, gears, bushes, etc. Studies are still being made to improve its impact and friction resistance as well as to lower its moisture absorption. Nylon-6 prepared from anionic polymerization distinguishes itself by simplicity of the process and relatively low temperature of polymerization. Polyether, polyester, ethylene propylene rubber and other polymers have been incorporated to modify it with some success^[1]. Polyorganosiloxane (POS) having highly flexible chain, very low T_g , high thermal stability and low surface energy would be a good substance for nylon modification. But the incompatibility of these two polymers makes it very difficult to be incorporated. A number of attempts have been made, for example, heat treatment of plastics with silicone oil^[2], ring-opening copolymerization of caprolactam (CL) and organocyclosiloxane^[3], block copolymerization of POS having carbon functional terminating groups with CL^[4a, 4b], sequent IPN of polyamide and POS^[5], etc. There exist difficulties such as hydrolytic stability of the product and complicity of the synthetic route in one or the other methods.

This paper provides a method of incorporating POS into nylon-6. It comprises a free radical addition of CL onto the vinyl group of POS and further anionic polymerization of the resulting macromer with CL.



where TDI denotes toluene diisocyanate and PA denotes polyamide part of product. By this scheme the C-H bond α to NH group of CL will take part similarly in addition, too.

The bulk and surface properties of the plastics are described and discussed.

EXPERIMENTAL

1. Preparation of vinyl-containing polydimethylsiloxane (PVMDMS)

One mole octamethylcyclotetrasiloxane and 1% mole of tetravinyltetramethylcyclorosiloxane were copolymerized in the presence of 1% tetramethylammonium hydroxide catalyst. A required amount of hexamethyldisiloxane was added for regulating the molecular weight. The viscosity of the obtained oil is about 200 cs. The vinyl group content determined by indirect coulometry is in accordance^[6] with the vinyl silicone added.

2. Addition of caprolactam to polyorganosiloxane

A mixture of 10 g of polydimethylsiloxane with 1% vinylmethylsiloxo linkage, 1 g of di-*t*-butyl peroxide and 9 ml of toluene was added slowly to 100 g of molten CL at 160°C under nitrogen atmosphere. Heating was maintained for several hours. The mixture was poured into water to separate the unreacted CL. The oil layer was dissolved in 10 ml of hexane and washed repeatedly with water. A semi-solid left after the solvent was thoroughly removed at reduced pressure. IR showed absorption at 3200 cm^{-1} (NH), 1660 cm^{-1} (C=O), 1053 — 991 cm^{-1} (SiO), 1252 cm^{-1} (SiCH₃) indicating the presence of CL group. Elemental analysis showed the presence of 1.3% nitrogen.

3. Anionic polymerization of caprolactam in the presence of PVMDMS

One hundred parts of CL was mixed with required amount of PVMDMS and 0.5% parts of 2,5-di-*t*-butylperoxy-2,5-dimethylhexane (that was used instead of di-*tert*-butylperoxide to avoid volatilization in the subsequent treatment). The mixture was heated to melt under reduced pressure at 100°C for 30 min to remove the absorbed moisture and heated at 120°C for 1 h and then 0.5% parts of sodium hydride was added, followed by 0.5% parts of toluene diisocyanate. The whole mixture was poured into a preheated mould and put into an oven at 180°C. The melt polymerized quickly, solidified in a few min and was allowed to stand there for 30 min. A light yellow polymer product was obtained.

By means of the above method polydimethyldiphenylsiloxane and polydiethylsiloxane with a few vinylmethylsiloxo linkages (PVMDPDMS, PVMDDES) have been incorporated to nylon-6 successfully to give similar polymers.

4. Test of bulk properties

The densities of the modified nylon-6 was determined on ASTM D792 in kerosene using a circular sample of 3 mm thickness, and the hardness on ASTM D785 with a Brinell Durometer, type PAB-625 on a board of 8 mm thickness. The tensile strength and ultimate elongation were determined on ASTM D638-84, sample V, directly casted from a dumbbell-shaped mould and sawn to 3 mm thickness. The hydrolytic stability of the polymers was also tested by its decrease of tensile strength after boiling with water for 24 h and drying at 105°C for 2 h. The impact resistance was determined on ASTM D256-84 with notched Izod sample. DTA graphs were recorded with a heating rate of 10°C/min.. T_m was taken from the first heating, T_c from natural cooling and T_g from second heating of the solidified sample so as to ensure better contact with the sensor sample holder. The SEM picture was taken from the fracture surface of the sample broken in liquid nitrogen.

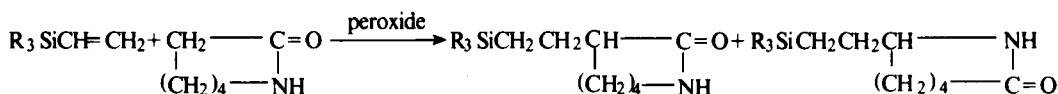
5. Test of surface properties

The contact angle of the surface was measured with contact goniometer MY-612S using water as wetting agent. Composition of the polymer sample taken from the surface and from the interior was determined separately by elemental analysis. The coefficient of friction and wear were obtained on a friction tester MHK 500 with an appropriate load and speed. The duration of coefficient of friction test is 10 min and that of wear lasts 1 h.

RESULTS AND DISCUSSION

1. Addition and polymerization

Free radical addition of a reagent to olefin to form carbon-carbon bond is a well-known reaction^[7]. The addition of caprolactam to vinyltrimethylsilane and vinyltriethoxysilane at elevated temperature has been reported by Nikishin^[8] and then by Mironov^[9] with the following scheme



R = Me, C₂H₅O

The hydrogen atoms on both carbon atoms alpha to >C=O and >NH group are activated to the radical addition. The total yield of the addition products is not high (<40%) because of polymerization of the vinyl group. In the present study the addition of CL to vinyl group of POS should proceed preferably and polymerization is suppressed by using large excess of CL. This has been verified by isolation of the addition product (Exp. 2). The CL group attached to siloxane chains will be able to partake anionic polymerization along with CL molecules in the usual way. Some branching or crosslinking product would be formed. However, under the given condition, low vinyl content in POS and small amount of peroxide added, the crosslinking would be very slight and the polymerized product could be melted to give a turbid liquid.

A silicone gel would result on the stage of radical addition when high vinyl content in PVMDMS or larger amount of peroxide was used. On the other hand, if PVMDMS was added to CL without peroxide and the mixture was anionically polymerized, a plastics was obtained, on its surface oily substances diffused out gradually and the mechanical properties were quite different, too (see below).

2. Bulk properties

The density of the modified nylon-6 decreases with the increase of silicone content and is always higher than the value calculated from linear additivity of two polymers (Fig. 1). It means that some sort of crosslinking has taken place.

Table 1 shows the dependence of hardness, tensile strength, ultimate elongation and impact resistance of the modified polymer on PVMDMS content. Incorporation of flexible polymer should lower the strength but in fact it is not so, provided the siloxane content does not exceed 5%. On account of slight crosslink formation the effect of soft polymer incorporation would be offset. For the same reason the impact resistance did not increase as expected. It is seen that

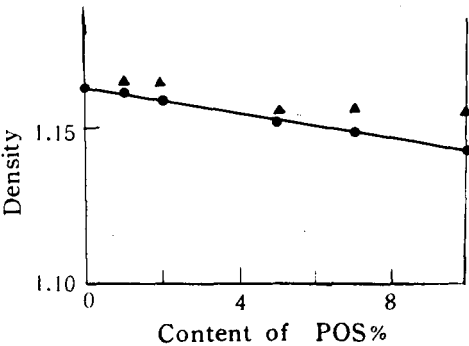


Fig. 1 Densities of the modified nylon-6
(▲) Observed values
(—) Calculated from additivity

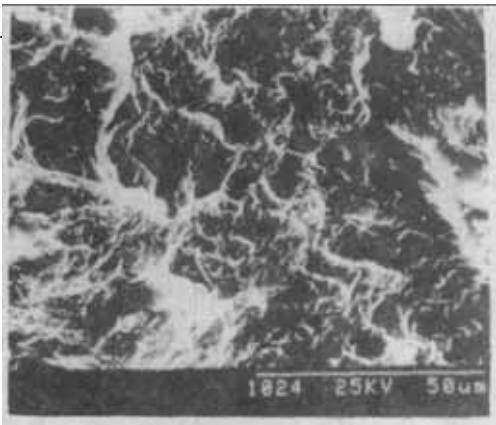


Fig. 2 SEM graph of nylon-6

Table 1 Properties of the modified nylon-6

PVMDMS content, %, wt/wt	0	2	5	7	10
Hardness, Brinell	8.5	7.2	8.5	7.8	7.6
Tensile strength, MPa	77.4	78.6	74.9	70.6	63.9
Ultimate elongation, %	25	19	18	26	27
Notched Izod Impact, J/m	35	27	45	34	35
T_m (°C)	222	222	222	223	222
T_c (°C)	191	191	190	191	191
T_g (°C)	73*	67	64	56	48
$T_c - T_g$, (°C)	114	124	126	136	143
Contact angle (°)	44	71	66	88	83

* Value of this sample obtained in the presence of peroxide.



Fig. 3 SEM graph of nylon-6 modified with 5% PVMDMS

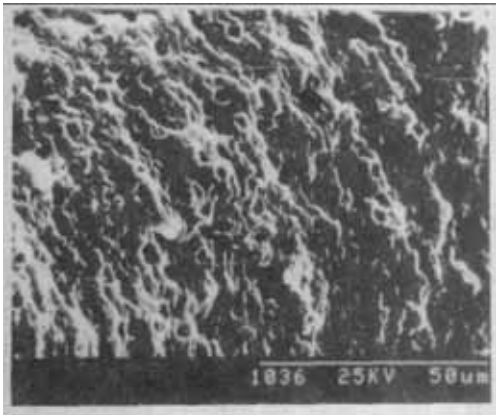


Fig. 4 SEM graph of nylon-6 modified with 10% PVMDMS

all the mechanical properties became worse as PVMDMS content is over 10%. On the other hand, it has been shown that the effect of peroxide is essential to the strength of the plastics since the tensile strength will be 12% lower for the

polymer blend obtained without the addition of peroxide for a sample containing 5% PVMDMS.

As a result of free radical addition the silicone atom is linked to amide group through three carbon atoms (see the above scheme). This linkage is generally considered to be hydrolytically stable. The hydrolytic stability of the present product was tested by reduction of its tensile strength upon long boiling with water. The plastics remains useful since only a reduction of 17% was observed for the sample containing 5% PVMDMS. The strength reduction of PVMDPDMS modified sample is much less at the same condition.

The SEM graphs show little difference between the nylon-6 control and that modified by 5% PVMDMS, whereas black spots are clearly seen on the fracture surface of nylon-6 modified by 10% PVMDMS. The result implies that phase separation occurs due to self-crosslinking of PVMDMS when it is added in greater amount.

The effect of PVMDMS content on thermal properties of the polymer was demonstrated by DTA, Table 1. It is seen that the melting point and temperature of recrystallization of the modified plastics do not vary appreciably no matter how much silicone has been incorporated whereas the T_g values decrease significantly with the increase of silicone content. It means that structural modification takes place mainly in the amorphous region. The difference of $T_m - T_g$ is considered as an index of crystallizing ability of a polymer^[10]. The higher the difference is, the more difficult the recrystallization will be. Increase of silicone content affords more possibility for intermolecular crosslinking of the two polymers and extends the amorphous region so that the crystallizing ability decreases accordingly.

4. Surface properties

POS is very flexible and incompatible with many other polymers. When they are incorporated together POS will be expelled outward to the surface^[11]. Composition analysis of the modified nylon-6 demonstrates that the sample from the surface has carbon and nitrogen content somewhat lower than that taken from the interior. A sample containing 10% PVMDMS gives typical values as follows:

Element	Calculated for CL	Sample from surface	Sample from interior
Carbon	63.73	60.96	61.66
Hydrogen	9.73	9.55	9.52
Nitrogen	12.39	11.40	11.61

Contact angle measurement also indicates that hydrophobicity increases with the increase of PVMDMS content that reveals the concentration of PVMDMS on the surface.

In view of the flexibility and thermal oxidative stability of POS, it would be able to improve the frictional and wear resistance of the polymer by incorporation. It is the case indeed. As reported by Owen^[4a], incorporating 2% of the polyamide-polydimethylsiloxane block copolymer (that was synthesized from a complicated route) to the molten polyamide could reduce the kinetic coefficient of

Table 2 The effect of polyorganosiloxane on the frictional properties of modified nylon-6
(load, 37.7 kg; speed, 500 r. p. m.)

Silicone content %	0		2		5		10	
	μ	w^*	μ	w	μ	w	μ	w
PVMDMS	0.37	S.M**	0.22	13.8	0.18	1	0.04	7
PVMDPDMS			0.15	5	0.11	1	0.11	2
PVMDES			0.13	S.M	0.10	S.M	0.10	S.M

* w is the loss in mg after friction of a sample of $12.3 \times 12.3 \times 19$ mm for 1 h.

** S.M : Surface melts

friction significantly. The same result can be obtained from the present simple method. The data on Table 2 show that both the coefficient of friction (μ) and wear (w) of nylon are reduced when POS has been incorporated. The value μ decreases with the increase of silicone content but the value w is found optimum as 5% or so of POS was incorporated. For PVMDES modified sample, surface melting takes place at high speed of friction although the μ value remain low. A more detailed study on its friction properties will be published soon.

Keyword:

Nylon; Silicone; Radical addition; Friction.

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