# Thermal characteristics of chitin and hydroxypropyl chitin

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The thermal properties of chitin and hydroxypropyl chitin (HPCH) were examined. Hydroxypropyl chitin was prepared from chitin and propylene oxide. The structure of HPCH was confirmed by solid-state $^{13}C$ nuclear magnetic resonance and Fourier-transform infra-red spectroscopy. From the results of elemental analysis, the degree of substitution was revealed to be about 0.8. As hydroxypropyl moieties were introduced on the C6 position in chitin, the solubility of HPCH in many organic solvents was enhanced compared with that of chitin. The dynamic mechanical analysis (d.m.a.) technique was employed to ascertain the glass transition temperature ($T_g$) of chitin and HPCH. The $\alpha$ transition peak of cast chitin and HPCH film by d.m.a. was observed at 236 and 252°C, respectively. Considering that rigid-rod-type polymers show $T_g$ followed by rapid thermal degradation, it was proposed that these temperatures should be $T_g$. Moreover, $\beta$ relaxation peaks were detected at ca. 143°C attributed to the presence of acetamide groups in chitin. In the d.m.a. spectra of HPCH, a new $\tan\delta$ peak, $\beta_2$ relaxation behaviour, was found at 105°C, probably due to the relaxation of the hydroxypropyl moiety in HPCH. Weight loss by thermogravimetric analysis implied that the relaxation above 250°C resulted from the decrease in modulus and was caused by thermal decomposition.

**(Keywords: chitin; hydroxypropyl chitin; thermal properties)**

## INTRODUCTION

Chitin, which is obtained from the cuticle of the marine crustacean, has recently aroused great interest on account of its industrial and biomedical applications[1]. Although chitin is naturally abundant, it has a limited application owing to its poor solubility and reactivity. Attempts have been made to prepare chitin derivatives to overcome the solubility problem. Chitosan is the fully or partially deacetylated product of chitin. Since chitosan is soluble in acetic acid and other organic solvents, it has more applications compared with chitin. In some applications, however, chitin is favoured instead of chitosan because deacetylation processes are often accompanied by decreasing crystallinity and lower the mechanical strength of the virgin chitin.

Studies on the thermal characteristics of polysaccharides such as chitin and cellulose are often difficult to pursue primarily because of the difficulty in sample preparation and the thermal decomposition before $T_g$ and $T_m$ due to the presence of the rigid-rod backbone. In general, differential scanning calorimetry (d.s.c.) does not provide information on $T_g$ and $T_m$ of polysaccharides. Recently, Nishio *et al.* reported the $T_g$ of cellulose containing dimethyl sulfoxide (DMSO) to be 208°C using the dynamic mechanical analysis (d.m.a.) technique[2,3]. In the mechanical relaxation studies of regenerated cellulose, a $T_g$ of ca. 250°C was reported in a torsional braid analysis[4]. Also, quite recently Manabe *et al.*[5] observed a broad, principal transition centred at ca. 240°C in the $\tan\delta$ measurement with a Rheovibron viscoelastometer using a high rate of heating (12°C min$^{-1}$) up to 330°C. As the cellulose is blended with polyvinylpyrrolidone (PVP), the decrease in the temperature of the onset of the transition particular to every blend was observed. Kakizaki *et al.*[6] have studied the molecular motion and relaxation behaviour of chitin, chitosan and related polymers in the temperature range from ca. −190 to ca. +100°C using dielectric analysis. For wet chitin, $\beta$ relaxation was detected at around −80°C. Bradley *et al.*[7] and Nishioka *et al.*[8] reported that $\gamma$ relaxation of cellophane, amylose and dextran is observed at around −90°C and at −40°C for chitosan.

Hydroxypropyl cellulose (HPC) has been known to form a liquid-crystalline phase[9–14]. We have prepared hydroxypropyl chitin (HPCH) following the procedure to prepare cellulose analogues[15], and found that they form a lyotropic mesophase. The glass transition temperature and more detailed molecular relaxation behaviour of chitin and hydroxypropyl chitin have not been reported. The objective of the present work is to study molecular motion and relaxation behaviour of chitin at elevated temperatures and to compare these results with those for related polysaccharides.

## EXPERIMENTAL

### *Materials*

The chitin sample was purchased from Tokyo Kasei Co. It was dried at 60°C under reduced pressure and kept in a desiccator over calcium chloride until used.

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Propylene oxide (Janssen Chemica) was stored at 4°C before use. Formic acid (extra-pure grade) was purchased from Junsei Chemical Co. Ltd.

### *Preparation of samples*

HPCH was synthesized from chitin and propylene oxide using 40 wt% aqueous NaOH solution as a catalyst (see *Figure 1*). First, 5 g of chitin (45–60 mesh), which was crushed by a roll-mill, and excess propylene oxide (77 ml), which also acts as a diluent, were stirred in an ice bath under reflux for 2 h. Then 3 ml of 40 wt% aqueous NaOH solution was added dropwise. The reaction vessel was heated up to 34°C with continuous stirring. The product, decanted in distilled water, was adjusted to pH 7.0 by adding HCl and filtered through a glass filter. After washing it with acetone and hot distilled water (80–90°C), the filtration was repeated several times. Finally, the product was dried at 60°C *in vacuo* for one day. Chitin and HPCH were dissolved in formic acid (99 wt%) at room temperature for 3 days to obtain 5% (w/v) polymer solution. Chitin and HPCH films were prepared by casting the solution on a glass plate and dried under reduced pressure over a period of 24 h. At least 0.2 mm in thickness is required for the dynamic mechanical thermal analysis.

### *Characterization*

Solid-state cross-polarization/magic-angle spinning (c.p/m.a.s.) $^{13}C$ n.m.r. spectra were obtained from a Bruker ARX-300 n.m.r. spectrometer operating at room temperature and at 4 kHz m.a.s. spin rate with 512 scanning number and 0.043 s of acquisition time. Elemental analysis (Carlo Erba, model 1108) was carried out at a combustion temperature of 1000°C and with a He flow rate of $100\,cm^3\,min^{-1}$. Degree of substitution (*DS*) was estimated in proportion to the relative contents of C, H and N in chitin and HPCH. A Fourier-transform infrared (*FT*i.r.) spectrometer (Nicolet, model 5DX) was employed to confirm the structure of HPCH. To compare the crystalline character of chitin with that of HPCH, wide-angle X-ray diffraction (WAXD) patterns were measured by the reflection method with nickel-filtered Cu $K_\alpha$ radiation using a Rigaku Denki X-ray diffractometer operated at 50 kV, 180 mA in the $2\theta$ scanning mode between 5° and 35°. Differential scanning calorimetric (d.s.c.) analysis was performed with a Du Pont Instruments 910 d.s.c. under $50\,cm^3\,min^{-1}$ nitrogen flow. D.s.c. thermograms of samples were taken from the second run. The dynamic storage modulus $E'$, loss modulus $E''$ and mechanical damping $\tan\delta$ were measured with a Du Pont Instruments 983 dynamic mechanical analyser (d.m.a.) at 1 Hz and 0.5 mm amplitude in an atmosphere of $200\,cm^3\,min^{-1}$ nitrogen. Instrument calibration could be accomplished through the d.m.a. calibration program. The dimensions of cast chitin and HPCH films were $1.22 \times 10.38 \times 0.21\,mm^3$ (clamping distance, width, thickness) and detailed length correction supplied the best measurement condition. Each sample equilibrated at 27°C was heated up to 130°C at a heating rate of $10°C\,min^{-1}$ and kept in an isothermal state for 3 min. After cooling, the temperature was raised at a rate of $5°C\,min^{-1}$ in the range 60–300°C. Thermal degradation of chitin and HPCH was characterized by a Du Pont Instruments 951 thermogravimetric analyser (t.g.a.) in the temperature range from 40 to 600°C at a programmed heating rate of $5°C\,min^{-1}$.

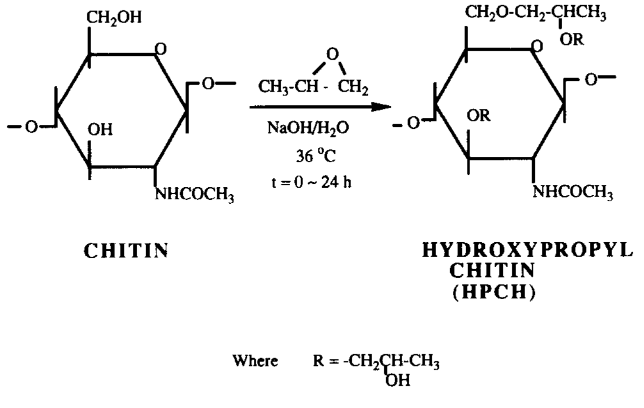

**Figure 1** Schematic of the preparation of hydroxypropyl chitin (HPCH)

## RESULTS AND DISCUSSION

*Figure 2* shows the solid-state $^{13}C$ n.m.r. spectra for chitin (a) and HPCH (b), respectively. From the comparison of spectra (a) and (b), the peak at 19.1 ppm in *Figure 2b* is assigned to be a $CH_3$ peak in the hydroxypropyl unit in HPCH. The broad peak detected at around 66.2 ppm is caused by the $CH_2$ and CH carbons in the hydroxypropyl unit.

*FT*i.r. spectra of chitin and HPCH (not shown here) show bands at around 1660, 1560 and $1420\,cm^{-1}$ for the chitin and at around 1664, 1561 and $1423\,cm^{-1}$ for HPCH, which have been assigned to amide I, II and III, respectively. In previous studies[16], there are two peaks in the amide I band in $\alpha$-chitin while there is only one band for $\beta$-chitin. Two peaks resulting from the amide I band were observed at 1660 and $1633\,cm^{-1}$ in chitin and at 1664 and $1632\,cm^{-1}$ in the case of HPCH, respectively. Accordingly, chitin and HPCH considered in this study are known to have $\alpha$ structure with antiparallel chains.

The intensity due to C–O stretching vibration of the primary alcohol at around $1025\,cm^{-1}$ became much smaller in HPCH than in chitin. The new peak that appeared at $2970\,cm^{-1}$ for HPCH indicated incorporation of the hydroxypropyl moiety. Since the primary alcohol is more reactive than the secondary alcohol, it seemed that the hydroxypropylation occurred primarily on the C6 position in the chitin backbone. Studies on the alkylation of chitin showed similar results as analysed by $^{13}C$ n.m.r. spectra[17]. HPCH was synthesized by varying reaction time from 6 to 24 h. Its *DS* was examined by elemental analysis. As listed in *Table 1*, *DS* values reached about 0.8 after 6 h of reaction time and no further increase of *DS* was seen after 6 h.

The X-ray diffraction pattern of chitin (*Figure 3a*) shows a maximum at around $2\theta = 9.8°$ and 19.5° due to the presence of (020) and the mixture of (110) and (040), respectively[17]. However, the relative peak intensity becomes smaller for HPCH (*Figure 3b*). It can be said that a decrease in hydrogen bonding force resulting from the bulky hydroxypropyl moiety apparently affects the decrease of the degree of crystallinity. As the degree of crystallinity decreases in HPCH, it is expected that HPCH may dissolve in organic solvents.

The thermal degradation patterns of chitin and HPCH were investigated using thermogravimetric analysis (t.g.a.)

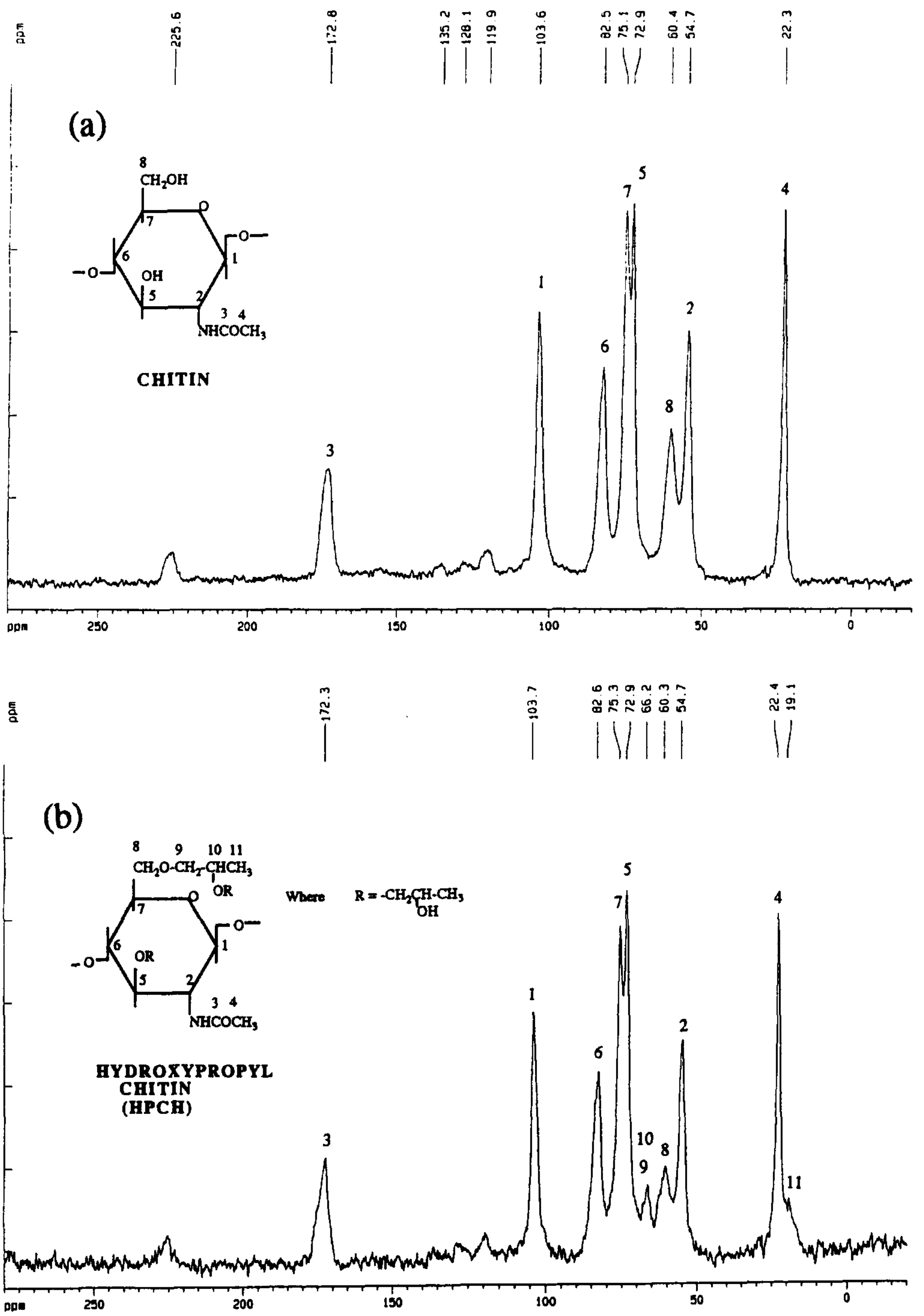

**Figure 2** Solid-state c.p./m.a.s. $^{13}C$ n.m.r. spectra of (a) chitin and (b) HPCH

**Table 1** Elemental analysis of chitin and HPCH

| Samples | Reaction time (h) | C (%) | H (%) | N (%) | Degree of substitution |
|---|---|---|---|---|---|
| Chitin | 0 | 41.7 | 5.92 | 6.06 | 0 |
| HPCH 6 | 6 | 47.5 | 7.11 | 5.36 | 0.82 |
| HPCH 12 | 12 | 46.6 | 6.95 | 5.54 | 0.80 |
| HPCH 18 | 18 | 46.6 | 6.75 | 5.51 | 0.80 |
| HPCH 24 | 24 | 47.4 | 7.16 | 5.27 | 0.82 |

and are given in *Figure 4*. Observable weight loss began above ca. 250°C, accelerated until an inflection point near 380°C and levelled off somewhat above ca. 400°C. The temperatures of 10% weight loss for both chitin and HPCH were determined to be at 287°C.

Differential scanning calorimetry (d.s.c.) was used to assess the thermal transition temperature of chitin and HPCH (not shown here). Cast chitin and HPCH do not show any features to which the glass transition can be related. They start to decompose at the onset of ca. 250°C. It is consistent with thermogravimetric analysis as shown in *Figure 4*. Therefore, it was difficult to detect the behaviour of molecular motion of chitin and HPCH by the d.s.c. technique. Polymers with a rigid-rod backbone such as cellulose and chitin are known to contain crystalline character, but the crystalline melting peak was not easily detected because they start to degrade even before the second-order transition temperature of these polymers[3].

In general, dynamic mechanical analysis is known to be more sensitive than calorimetric measurements for the

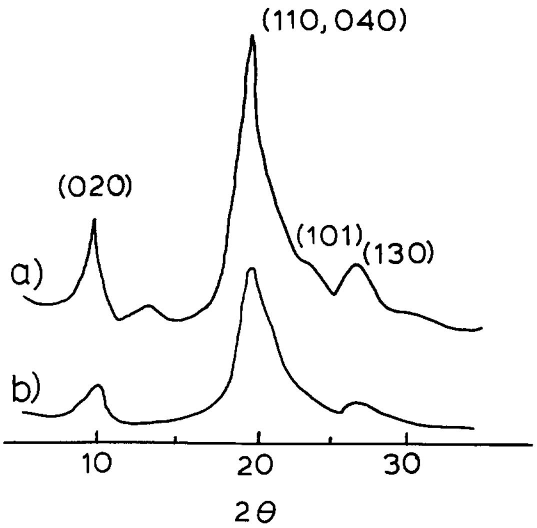

**Figure 3** X-ray diffraction patterns of (a) chitin and (b) HPCH

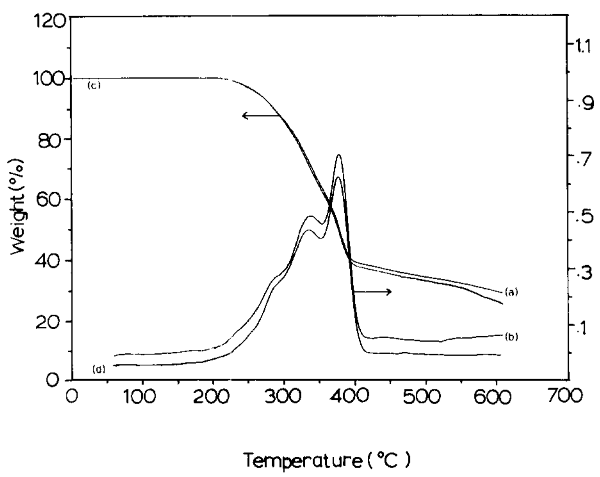

**Figure 4** (a) T.g.a. and (b) t.g.a. derivative thermograms of chitin, and (c) t.g.a. and (d) t.g.a. derivative thermograms of HPCH

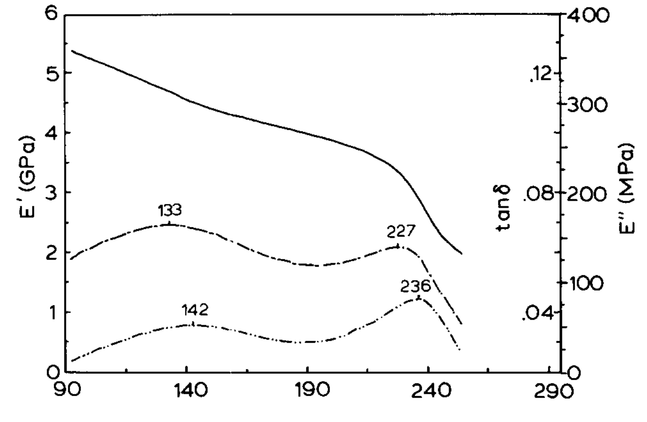

**Figure 5** D.m.a. relaxation spectra of chitin; $E'$(——), $E''$(— · —) and tan $\delta$(— ·· —)

detection of $T_g$. Accordingly, we measured the dynamic mechanical relaxation spectra of chitin and HPCH, hoping to find their glass transitions. The results are given in *Figures 5* and *6*.

In *Figure 5*, cast chitin film showed the tan $\delta$ maxima at 143 and 236°C. The transition at 236°C is possibly the $T_g$ of chitin. Considering that the dynamic storage modulus of chitin is ca. 3 GPa, it can hardly be said that the tan $\delta$ maximum value appearing at 236°C is a transition due to the degradation of chitin. In fact, chitin starts to degrade at ca. 250°C from t.g.a. analysis (*Figure 4*). The loss modulus ($E''$) maxima appeared at 133 and 227°C. The relaxation peak appearing at 143°C in the tan $\delta$ curve is caused by the acetamide group attached to the C2 position in chitin, since the acetamide group is bulkier than the methylol unit and sterically hindered.

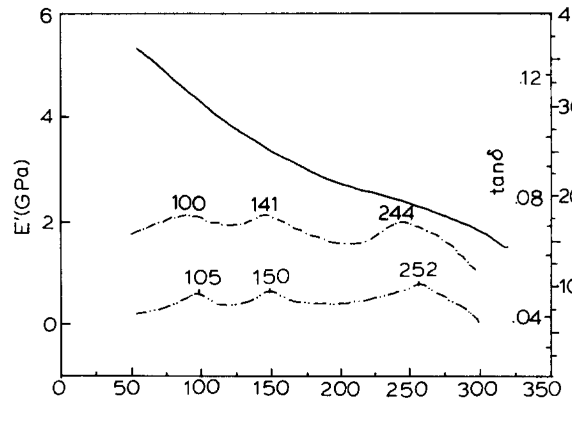

**Figure 6** D.m.a. relaxation spectra of HPCH; $E'$(——), $E''$(— · —) and tan $\delta$(— ·· —)

*Figure 6* illustrates the d.m.a. relaxation spectra of HPCH. The $\alpha$ transition peak appeared at 252°C. The second relaxation peak in the tan $\delta$ curve is observed at ca. 150°C. Both of these two relaxation temperatures are about 8–16°C higher than those of chitin. Another noticeable difference between the tan $\delta$ curves of chitin and HPCH is the third relaxation maximum for HPCH (*Figure 6*) at ca. 105°C and assigned to be $\beta_2$ relaxation. Considering the fact that the sample is well dried, $\beta_2$ relaxation is believed to appear due to the presence of the hydroxypropyl group in HPCH.

The increased transition temperatures of HPCH compared with chitin can be explained by molecular flexibility, not size, owing to the substitution of side groups onto a polymer chain. Molecular flexibility is limited by the bulky hydroxypropyl group, and local relaxation of HPCH main chains is restricted to some extent. By Manley *et al.*'s work mentioned before[2,3], when poly(vinyl alcohol) (PVA) is blended with cellulose, the relaxation peaks of PVA in tan $\delta$ and $E''$ shift to higher temperature with a decrease of degree of crystallinity. This behaviour implies that the local relaxation of PVA main chains becomes restrained and the $T_g$ is elevated by adding cellulose.

We can compare these transition temperatures and relaxation behaviour with polysaccharides and the comparisons are made as listed in *Table 2*. In the mechanical relaxation studies of regenerated cellulose, a $T_g$ value of ca. 250°C was reported in a torsional braid analysis[4]. Also quite recently, Manabe *et al.*[5] observed a broad, principal transition centred at ca. 240°C in the tan $\delta$ measurement with a Rheovibron viscoelastometer using a high rate of heating (12°C min$^{-1}$) up to 330°C. Nishio *et al.*[2] reported that cellulose containing DMSO showed a $T_g$ of 208°C. As the cellulose is blended

**Table 2** Relaxation behaviour of various dry natural polymers

| | Relaxation temperature (°C) | | | | |
|---|---|---|---|---|---|
| Polymers | $\alpha$ | $\beta_1$ | $\beta_2$ | $\gamma$ | References |
| Chitin | 236 | 142 | | −50 | This study |
| HPCH | 252 | 150 | 105 | | This study |
| Chitosan | 150 | | | −40 | 6, 7 |
| Amylose | 200 | 100 | | −75 | 6, 7 |
| Dextran | | −80 | | | 6, 7 |
| Cellulose | 208 | | | | 2 |
| Cellophane | 195 | −50 | | −90 | 7 |

with polyvinylpyrrolidone (PVP), a decrease in the temperature of the onset of the transition particular to every blend was observed.

## CONCLUSION

From chitin and propylene oxide, HPCH was synthesized by introducing hydroxypropyl moieties into the C6 position in chitin. The estimation of degree of substitution by elemental analysis, solid-state $^{13}C$ n.m.r. spectra and *FT*i.r. measurements confirmed hydroxypropylation of chitin. No transitions in chitin and HPCH were found by differential scanning calorimetry. Dynamic mechanical analysis showed $\alpha$ transition temperatures of chitin and HPCH, that is, glass transitions due to relaxation of polymer main chain, at 236 and 252°C, respectively. It was deduced that the local relaxation of the HPCH main chain was restricted by the bulky hydroxypropyl unit. The $\beta$ relaxation of chitin was detected at 133°C and shifted to 142°C in HPCH. A peak appearing at 105°C in the d.m.a. spectra of HPCH was assigned to be $\beta_2$ relaxation. Thermogravimetric analysis revealed that chitin and HPCH showed a $T_g$ followed by rapid thermal degradation.

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