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Paper

Chemical Interaction in β-Tricalcium Phosphate/Copolymerized Poly-L-Lactide Composites

Masanori KIKUCHI and Junzo TANAKA

National Institute for Research in Inorganic Materials, 1-1, Namiki, Tsukuba-shi, Ibaraki 305-0044

β リン酸三カルシウム/ポリ乳酸共重合体複合体中の化学的相互作用

菊池正紀・田中順三

無機材質研究所, 305-0044 茨城県つくば市並木 1-1

For the development of a novel biodegradable membrane useful for surgical operations, the chemical interaction between β-tricalcium phosphate (TCP) and copolymerized poly-L-lactide (CPLA) in the TCP/CPLA composites was investigated by Fourier-transformed infrared spectroscopy (FT-IR) and dynamic mechanical analysis (DMA). From FT-IR measurements, chemical interaction between Ca^{2+} in TCP and $O^{\delta-}$ of ester C=O double bonds in CPLA was detected as the red shift of C=O stretching vibration mode. DMA measurements showed that the storage and loss elastic moduli of the composites increased with increasing in TCP content, corresponding to the strength change in $Ca^{2+}...O^{\delta-}(=C^{\delta+})$ interaction, though glass-transition and softening temperatures did not change. The mechanical and thermoplastic properties of the composites were highly suitable for a guided-bone-regeneration membrane.

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1. Introduction

Hydroxyapatite (HAp) and β-tricalcium phosphate (TCP) are well known as bioactive and biocompatible materials which can directly bond with bone and/or conduct bone tissues along the surfaces.[1] Though these properties are very suitable for bone substitute, their brittleness is a fatal weak point for application as structural biomaterials; therefore, they are only used as fillers or metal-coating materials. Some synthetic polymers are currently used as biodegradable sutures (polyglycol acid) or bone plates (poly-L-lactide)[2),3] which need no secondary operation to be removed after healing; however, they are not biocompatible or bioactive.

Recently, some composites of HAp and biodegradable polymers have been synthesized. For example, lactic acid oligomer was impregnated into a porous HAp ceramic to enhance fracture toughness;[4] then, the osteoconductivity improved but the fracture toughness was not sufficient for bone substitution. Chen et al.[5] investigated the osteoconductivity of a similar composite at cranium for 12 weeks; however, the composite had no osteoconductivity. Moreover, Tencer et al.[6] prepared new composite materials using coral HAp which had the similar osteoconductivity to Ref. 4). Jansen et al.[7] synthesized a poly(ethyleneglycol terephthalate)/poly(butylene terephthalate) composite sheet coated with HAp powder which was used for guided bone regeneration (GBR). However, the medical application of these composites is limited, as they cannot be easily formed into suitable shapes for surgical operations.

The authors prepared novel TCP/CPLA (copolymerized poly-L-lactide[8]) composites using a heat kneading method; the composites showed no cytotoxicity and had nearly the same mechanical properties as bone.[9),10] In this study, a chemical interaction between TCP and CPLA in the composite was investigated by Fourier-transformed infrared spectroscopy (FT-IR) and thermoplasticity was estimated by a dynamic mechanical analysis (DMA) to elucidate the origins of the mechanical and thermoplastic properties of the composites.

2. Materials and method

TCP powder was prepared by a conventional wet method using $Ca(OH)_2$ and H_3PO_4 as starting materials and heated at 1073 (TCP_{1073}) or 1373 K (TCP_{1373}). The powder obtained was ground to 125 μm or less in radius of secondary particle. Two types of CPLA, soft type (CPLA-S) and hard type (CPLA-H), were prepared by the copolymerization of poly-L-lactide and polyethylene sebacate. Mixing ratios of TCP/CPLA composites are shown in Table 1. The TCP/CPLA composites were prepared by a heat kneading method with a mill (Laboplastomill, Toyo Seiki Co.); immediately after CPLA was melted in the mill at 453 K, TCP powder dried at 453 K for 10 min was added into the mill and mixed at 453 K for 10 min at 20 rpm. The composite was cooled to room temperature in air and formed into a plate by heat pressing.

A chemical interaction between TCP and CPLA was investigated by FT-IR reflectance measurements; especially, the stretching mode of ester C=O bond in CPLA, found around 1770 cm^{-1}, was measured in detail at a scanning resolution of 0.2 cm^{-1} and with incident/reflection angles of 60, 75 and 85°. Here, TCP/CPLA-H composites were used for the measurements since a small amount of co-esters in CPLA-S inhibits red shift of IR spectra. Thermoplastic properties were evaluated by storage and loss modulus, measured by a dynamic thermomechanometry (DMA; Solid Analyzer RSA II, Rheometrics Inc.) at a tensile frequency of 1 Hz; for these measurements, TCP/CPLA-S composites were used.

Table 1. Mixing Ratio of TCP/CPLA Composites

	TCP content /mass%				
	25	50	75	85	90
CPLA-H	—	√	√	√	√
CPLA-S	√	√	√	—	—

√: prepared and —: not prepared.

3. Results and discussion

A scanning electron micrograph of fracture surface of TCP/CPLA composite shown in Fig. 1 indicated that TCP and CPLA were mixed homogeneously in the composite and were well-adhered each other. Figure 2 shows the FT-IR spectra of composites which were converted from measured reflectance spectra with Kramers-Kronig relations. Stretching vibration bands due to an ester C=O double bond were observed around 1770 cm^{-1} for all samples. In the spectra measured with a reflection angle of 60° (left side), the chemical shift of the C=O stretching band was not obviously detected. When the reflection angle increased to 75° (middle side), however, the samples showed a clear chemical shift except for a composite with TCP_{1073}/CPLA=50/50. Then, the C=O band split into two subbands for 85/15 and 90/10 composites, and the chemical shift of the subbands increases with the TCP_{1073} amount. At a reflection angle of 85°, the chemical shift was observed even in the 50/50 composite; however, the C=O band was not apparent with the other samples.

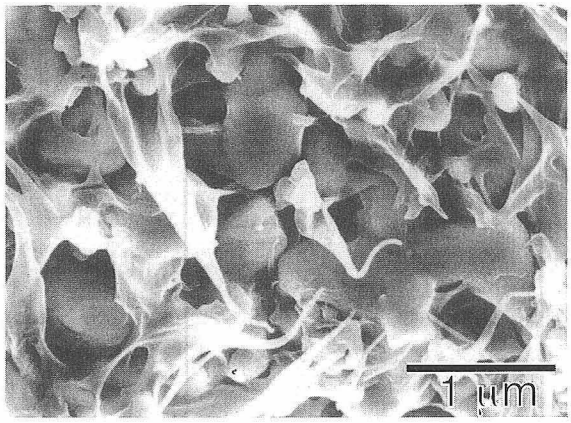

Fig. 1. Scanning electron micrograph of fracture surface of TCP/CPLA composite.

Since the increase in reflection angle enhances the IR signals just around TCP-particle/surrounding-CPLA interfaces due to a multiple reflection effect, the IR spectrum behaviors seen in Fig. 2 indicated that the C=O stretching vibration at the interface shifted to lower wave number with increasing TCP. In general, the decrease in chemical bond strength results in the decrease in vibration frequency; i.e., a red shift can be found. As the C=O stretching mode at the TCP/CPLA interface showed the red shift as a function of TCP amount, a weak chemical bond was considered to form between Ca ions on the TCP surface and slightly polarized O atoms of ester C=O bonds in the surrounding CPLA. The formation of the chemical bond causes the adhesive property of TCP and CPLA. In general, the adhesion strength between two substances is ascribed mainly to mechanical lock and chemical bond. The mechanical lock in micro range depends on contact angle, i.e., adhesion tension, because substance having a large contact angle cannot infiltrate micropores on the surface of substrate. Hence, chemical bond in relation to adhesion tension is very important factor to determine the adhesion strength. The reason why the mechanical strength of general organic/inorganic composites decreases with increasing in inorganic filler content is caused by no interaction between covalent organic and ionic inorganic substances. Therefore, the present TCP/CPLA composites having the chemical bond between TCP and CPLA indicated almost constant mechanical strength up to more than 50% of TCP amount. No apparent chemical shift was observed for the composite with TCP_{1373}/CPLA-H=75/25; this phenomenon was ascribed to a large primary particle size of TCP_{1373}, typically 2–3 μm, being much larger than that of TCP_{1073} of 200–500 nm.

Figures 3 and 4 show storage (E') and loss (E'') modulus curves for TCP/CPLA-S composites as a function of TCP content; the resultant E'-values at 293 K (E'_{293}) are given in Table 2 together with glass transition temperatures (T_g) and softening temperatures (T_t). T_g and T_t were almost constant while E'_{293}, an indicator of elastic modulus, increased with the increase in TCP content. Both E' and E'' curves shifted to a high modulus side with increasing TCP content, and double peaks of E'' converged then into

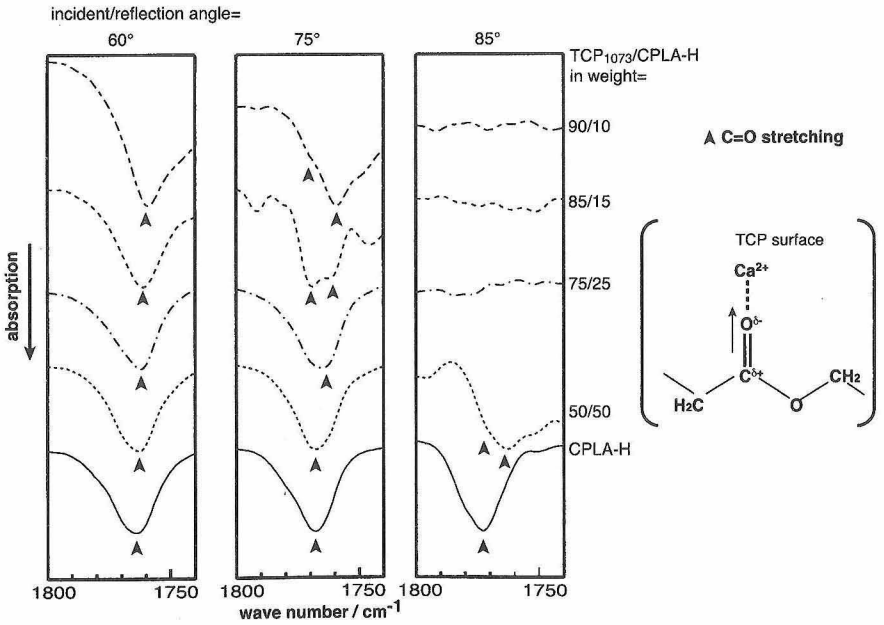

Fig. 2. Fourier-transformed infrared spectra of TCP/CPLA composites. Absorption bands in this figure are ascribed as C=O stretching bond of ester in CPLA.

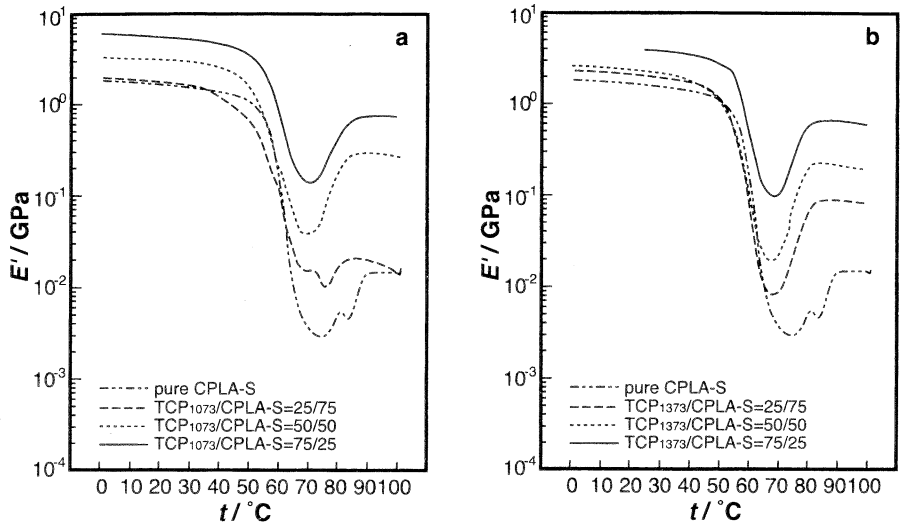

Fig. 3. Storage modulus curves of TCP/CPLA-S composites for different TCP content as a function of temperature.

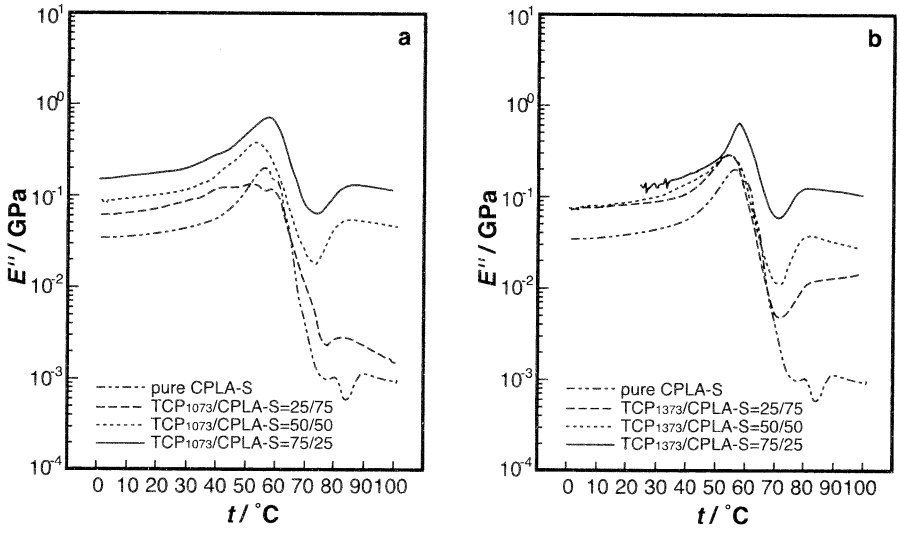

Fig. 4. Loss modulus curves of TCP/CPLA-S composites for different TCP content as a function of temperature.

Table 2. E' at 293 K, T_g and T_t of TCP/CPLA Composites

Composite	TCP /mass%	E'_{293} /GPa	T_g /°C	T_t /°C
CPLA-S	—	1.63	56.0	55.1
TCP_{1073}/CPLA-S	25	1.87	56.6	49.9
	50	3.27	52.0	47.9
	75	5.67	57.1	50.4
TCP_{1373}/CPLA-S	25	2.08	53.3	50.5
	50	2.45	53.8	49.6
	75	3.85	57.4	53.8

single peak. That was, the TCP/CPLA composite softened one step and the pure CPLA softened two steps. The softening mechanism of thermoplastic polymers, including CPLA, is considered as releasing of molecules themselves from bonding force (van der Waals' force) by Brownian motion. So, they can transform when the part of the molecules becomes free from the bonding force. In the TCP/CPLA composites, CPLA was fixed to TCP via the chemical interaction between TCP and CPLA. Hence, the composites with high mixed ratio of TCP cannot transform until all the CPLA molecules became free from bonding force between TCP and CPLA as well as between CPLA molecules because TCP cannot transform at these temperature and load. Consequently, softening of the TCP/CPLA composite was detected as one step. Softening temperature did not have an increasing trend with TCP amount mixed in the composites. All T_t, around 50°C, so the surgeon can touch and transform the composites as required at chair-side.

These results suggested that TCP and CPLA in the composites formed chemical bond which was sufficiently weak not to change their softening temperature but was sufficient for keeping their mechanical strength.

4. Conclusion

Interaction between TCP and CPLA in the TCP/CPLA composites, prepared by a heat kneading method, was observed with FT-IR. This interaction was considered as a weak ionic bond between Ca on the TCP surface and O of

ester double bond in the CPLA molecules. The bond could keep mechanical strength of the composite when TCP volume ratio in the composite was in excess of 50%. The results from DMA also indicated the existence of chemical bond between TCP and CPLA and a good ability for application as a thermoplastic artificial bone material.

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